EXPERIMENTAL INVESTIGATION OF PROCESS INDUCED STRAIN DURING CURE OF EPOXY USING OPTICAL FIBRE BRAGG GRATING AND DIELECTRIC ANALYSIS

Ulrich A. Mortensen[1], Tom L. Andersen[2], Jacob Christensen[1], Marco Aurelio Miranda Maduro[2]

[1]Department of Wind Energy, Section of Composite Mechanics and Structures, Technical University of Denmark, Risø Campus, Frederiksborgvej 399 4000 Roskile, Denmark
Email: ulmo@dtu.dk
[2]Department of Wind Energy, Section of Composite Material, Technical University of Denmark, Risø Campus, Frederiksborgvej 399 4000 Roskile, Denmark
Email: mamm@dtu.dk

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Abstract

In order to investigate how cure cycles for composites can be optimized for improved fatigue life of composites, an experimental set-up which measures temperature, process induced strain and level of cure, is presented. The experimental set-up measures strain in a neat epoxy sample using optical Fibre Bragg Grating sensors in a single glass fibre, combined with a thermo-couple used to compensate for thermal effects. The degree of cure in the neat epoxy sample is measured in the same sample using a dielectric sensor working simultaneously with the temperature and strain measurements. The combined measurements allows for quantification of a number of important parameters required for understanding how the temperature profiles used in processing of composites affects the level of process induced strains in the neat polymer material and thereby the level of residual stresses in the final composite materials.

1 Introduction

Epoxy based thermoset resins are widely applied as matrix material for high performance fibre reinforced composites. Curing of resins during composite manufacturing induces chemical and thermal strains in the final composites product. Process induced residual strains are undesirable for a multitude of reasons, including shape distortion, warpage, spring-in effects and possibly impaired material properties. With regards to material properties, a recent study [1] found that the fatigue life performance of glass fibre reinforced polymers manufactured using non-crimp fabrics were improved when the process induced internal strains in the material were lowered.

The findings by Hüther yields the need for a sound experimental procedure to evaluate different cure cycles with respect to process induced strains, such a method is proposed in this work in an experimental set up that combines optical Fibre Bragg grating (FBG) sensors, measuremets using a Dielectric Analyszes (DEA) and a thermo-couple. FBG sensors have been applied for in-situ measurement of strain in thermoset epoxies [1, 2, 3, 4, 5, 6], and a few of them combines the strain measurement with cure kinetic modelling to show the effect of curing to the build-up of strain. Two previous works [5, 6] have combined Dielectric analysed measurements (DEA) with strain measurements by FBG, but none of the works converted the signal to a degree of cure or provided methodology for engineering application of their work. The purpose of the work reported here is to provide a sound methodology that combines exclusively

experimental measurements to evaluate the influence of epoxy on the build up of strains with a special focus on the meaning of the temperature of gelation of the epoxy.

2   Methodology

2.1   Experimental set-up
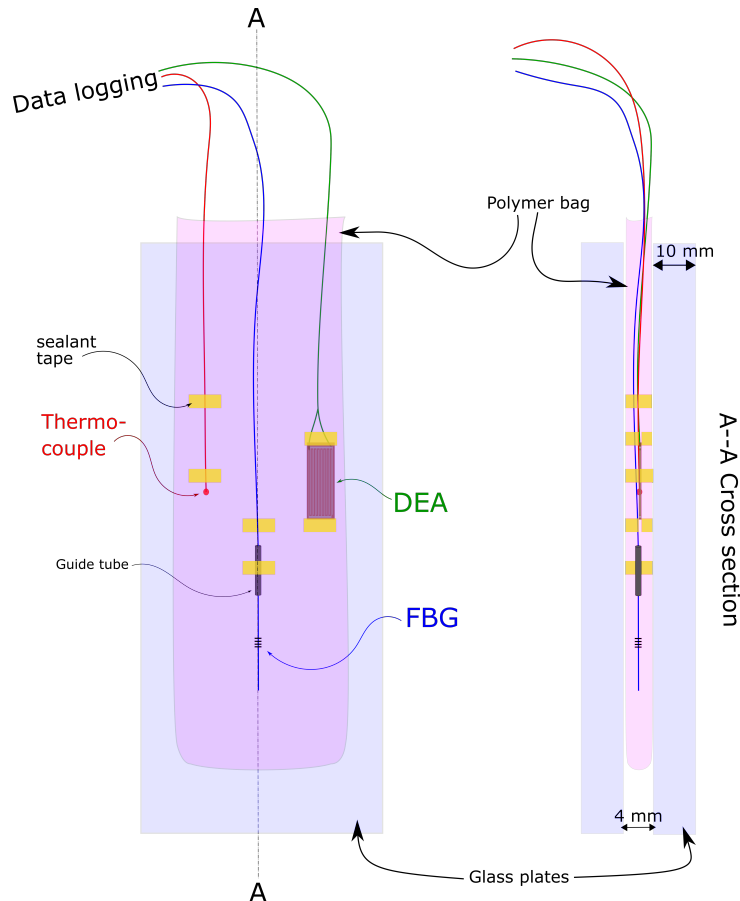
Figure 1: Schematic representation of the experimental set up

The experimental set up reported in this work takes some inspiration from the work of Hüther et al [1], but with significant changes – including the implicit measurement of the degree of cure of the epoxy by DEA – to the measurement. The most important of the changes is to the geometry. Both Hüther et al [1] and Prasatya [7] used cylindrical tubes with inner diameter of more than 1 cm, which in Hüthers case caused exothermic peaks that exceeded the target temperatures with more than 100 °C. Prasatya only reported the ambient oven temperature used to conduct the experiments.

Figure 1 schematically depicts the experimental set up, which includes the DEA sensor, the type K thermo-couple and the FBG sensor. The polymer bag, made from high temperature resistance nylon of 0.05 mm thickness, are sandwiched in between to 10 mm thick glass plates. The sensors inside the bag are fastened to the bag using rubbery sealant tape (normally applied for vacuum infusion moulding). The DEA sensor were mounted with two pieces of sealant tape where the wires are soldered to the sensor, and two pieces of sealant tape at the opposite end of the sensor, leaving the sensing area of the DEA sensor uninterrupted by the sealant tape. The thermo-couple sensor were likewise fastened by holding the two piece wire sandwiched between two pieces of sealant tape, but without the sealant tape interfering with

Ulrich A. Mortensen, Tom L. Andersen, Jacob Christensen, Marco Aurelia Miranda Maduro
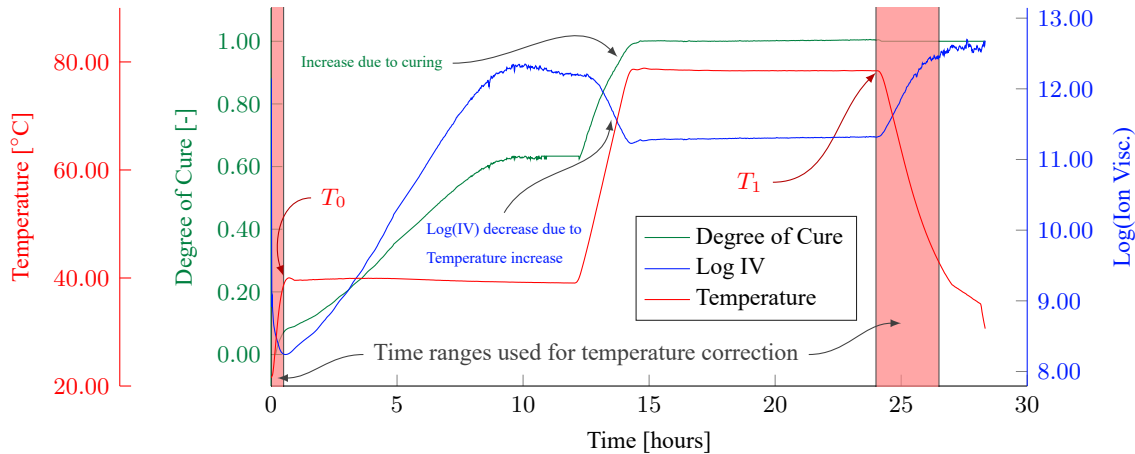
Figure 2: Two stage cure cycle C with holds at 40 C and 80 C. The temperature, Ion Viscosity (Logarithmic) and the Degree of Cure is plotted as functions of time. The red zones indicate the time range used to fit the temperature dependence of the logarithm of ion viscosity.

welded spot at which the temperature is effectively measured. The FBG sensor measures strain where bragg gratings have been inscribed in the fibre. The length of the bragg gratings in the applied FBG sensor is 5 mm. The sensor is fastened with sealant roughly 5 cm above the sensing area and then tunneled through a guide tube, also fastened between two pieces of sealant tape, such that the bragg gratings of the fibre starts 5-10 mm after the guide tube.

Two pieces of 4 mm thick spacers where used to control the thickness between the moulding glass plates. The sealant tape used to hold the sensors are squeezed by the glass plates causing points of friction with enough force to hold the bag vertically when filled with epoxy. Near the FBG sensing area the bag was free to move, and the maximum constraint of the epoxy shrinkage equates to the maximum friction forces that can exist between the bag and the glass tooling plates, and the resistance from the bagging material itself. The small thickness of the bagging (0.05 mm) compared to the total distance from the centrall located FBG sensor (2 mm away) means that the bag itself do not constrain shrinkage where measurements are made. The *maximum* theoretical friction force caused by the hydrostatic pressure of submersing the fibre into the initially liquid epoxy amounts to a negligible effect to the strain measurements of the FBG sensor.

2.2 Converting Dielectric properties to degree of cure

The ion viscosity signal obtained from the DEA are affected by change in cross-linking density but also by changes in the material temperature, regardless of the degree of cure. The relation to the polymer cross-linking means that the ion viscosity can be used as a measure of the degree of cure of the resin sample. The ion viscosity do however only provide the relative change in the degree of cure, which is also affected by the material temperature for all curing states of the resin.

Two steps are applied in converting the raw Ion viscosity signal into a degree of cure: temperature correction and signal normalization. First linear regression is used to find the relation between the $\log(IV)$ before curing starts and after curing ends. The coefficient for the thermal dependencies are denoted μ_{cured} and $\mu_{uncured}$, and the degree of cure is denoted c. Eq. (1) provides the assumption that the change in thermal dependency of the Log(IV) is linear between the uncured and the cured state. Equation (2) applies a normalization of the signal based on the values just as curing starts (end point of the first time range shown in Figure 2, T_0) and after curing (start point of the rightmost time range in Figure 2, T_1). Equation (3) makes a correction based on linear change in thermal dependency from the normalized signal

Ulrich A. Mortensen, Tom L. Andersen, Jacob Christensen, Marco Aurelia Miranda Maduro

combined with a linear dependency of the change in temperature from the T_0 and T_1 respectively.

$$\mu = \mu_{uncured} \left(1 - c\right) + \mu_{cured}c \tag{1}$$

$$\log(IV)_{norm} = \frac{\log(IV) - \min(\log(IV))}{\max(\log(IV)) - \min(\log(IV))} \tag{2}$$

$$\alpha = \log(IV)_{norm} - \left[(T - T_0)\,\mu_{uncured}\left(1 - \log(IV)_{norm}\right) + (T - T_1)\log(IV)_{norm}\mu_{cured}\right] \tag{3}$$

2.3   Strain from Optical Fibre Bragg Grating and Gel point definition

Strain measurements using optical fibre Bragg gratings have been reported in numerous previos works [1] [2] [4]. The optical fibres obtained from HBM sensing was produced with bragg Gratings causing wavelength peaks λ_b between 1500 nm and 1600. Equation (4) provides the wavelength shift caused by thermal and mechanical straining of the optic fibre. For the applied fibres the photo-elastic coefficient is $p_e = 0.22$, the thermo-optic coeffiecient is $\xi = 6.7 \cdot 10^{-6}$, thermal expansion coefficient is $\alpha_f = 0.55 \cdot 10^{-6}$ K^{-1}. A dip-coating procedure with epoxide functionalised organo silane [8] was applied to the fibres to simulate the interface bonding that exist in normal glass fibre reinforced epoxy polymers.

$$\Delta\lambda_b = \lambda_b \left[(1 - p_e)\,\varepsilon + ((1 - p_e)\,\alpha_f + \xi)\right] \tag{4}$$

The gel point is defined in this work as the material state where the resin can attain normal stresses at material temperature higher than the glass transition temperature of the material at the given point in time. The method proposed by Mikkelsen et al [3] is consistent with this definition and will be applied here. The definition is summarized in eq. (5), and it is noted the tolerance value δ used in this study is $2 \cdot 10^{-5}$ unless otherwise specified. It should also be noted that this work follows the assumption made by Mikkelsen et al [3] that after gelation of the resin, the thermal expansion of the fibre itself is neglected. This assumptions comes from the fact that the fibre is small (Ø125 μm) compared to the amount polymer that surrounds it, and thus the fibres strain will follow the polymer strain.

$$\varepsilon = \begin{cases} 0 & \text{if} \quad \frac{\Delta\lambda_b}{\lambda_b} - \left[(1 - p_e)\,\alpha_f + \xi\right]\Delta T < \delta \\ \frac{\frac{\Delta\lambda_b}{\lambda_b} - \xi\Delta T}{1 - p_e} & \text{if} \quad \frac{\Delta\lambda_b}{\lambda_b} - \left[(1 - p_e)\,\alpha_f + \xi\right]\Delta T \geq \delta \end{cases} \tag{5}$$

2.4   Applied temperature profile

Through DSC analysis the glass transision temperature T_g of the epoxy was found to be 84 °C at full cure. One of the suggested cure cycles by the manufacturer of the epoxy consists of an isothermal temperature hold of 80 °C for 8 hours. In order to ensure that all applied cure cycles resulted in a fully cured material, thus disallowing any further chemical shrinkage, all cure cycles had to meet the requirement of ending the cure with at least an 8 hour hold of 80 °C. The applied cure cycles are presented in Table 1, where they are categorized into *Two step* and *One Step* cures. The One step cures are resemblant of the high temperature cures suggested by the manufacturer. The two step cures are constructed with the goal of reaching gelation of the epoxy material at a low temperature where the epoxy cannot reach full cure. The second step in the two step cures were applied to reach full cure of the material.
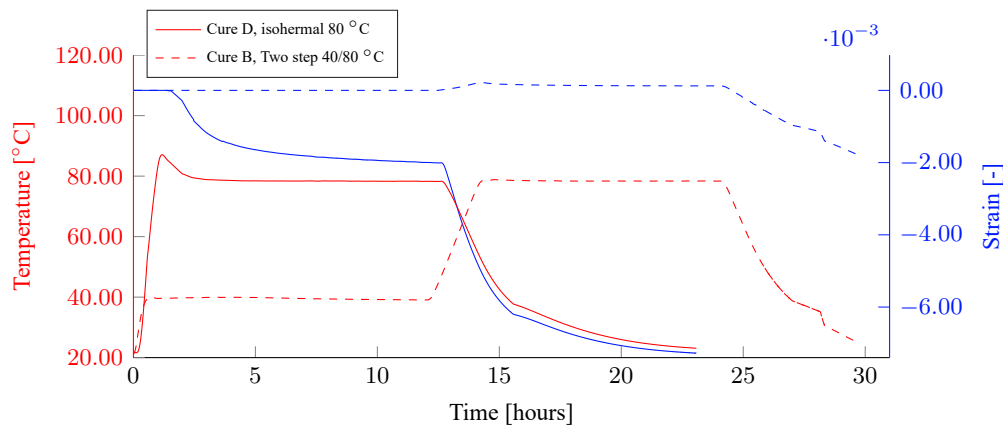
3   Results

Figure 3 shows two of the applied cure cycles. Cycle B is a two-step cure with a 40 °C hold and a 80 °C hold, while cure D is a one step cure with 80 °C. The strain development for Cure D shows a significant

Ulrich A. Mortensen, Tom L. Andersen, Jacob Christensen, Marco Aurelia Miranda Maduro

Table 1: Cure profiles investigated

Cure Name	Cure Type	Steps	
		Step 1	Step 2
A		30° C for 12 hours	80° C for 12 hours
B	Two step	35°C for 24 hours	80°C for 10 hours
C		40°C for 12 hours	80°C for 12 hours
D	One Step	80°C for 12 hours	
E		110°C for 8 hours	

amount of chemical shrinkage occurring early in the cure, and then a significant amount of thermal strain occurring during cool down. For cure B, the two step cure, the first non-zero strain goes into the tensile regime due to the thermal expansion of the gelled epoxy during the temperature increase to 80°C. During the temperature increase of Cure B the chemical shrinkage and thermal expansion are working in opposite directions and are to some degree cancelling each other out. The effect here is that at the end of the final step of 80°C the strain is positive, and after cool down the final strain ends a lower level than for the one step cure.
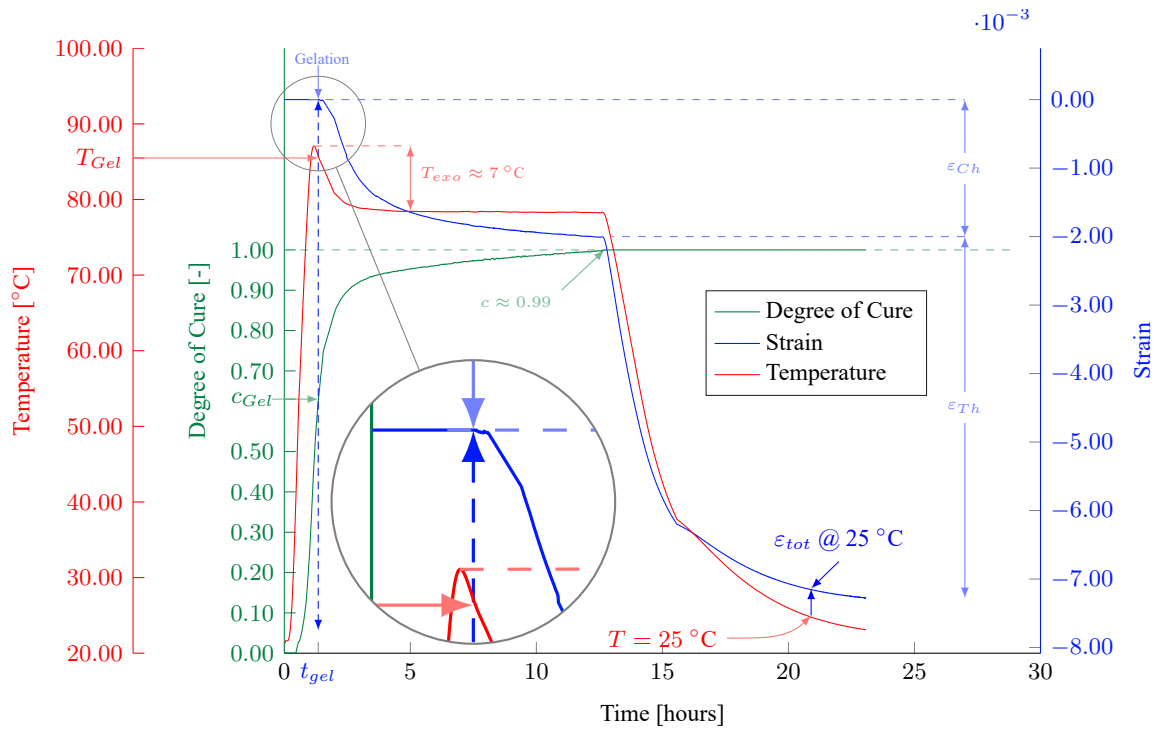

Figure 3: Temperature and strain development over time for two representative types of cure. Red lines are temperature and blue lines are strain. Cure B (two-step) is marked by dashed lines and Cure D (one-step) is marked by solid lines.

The results for each of the cure cycles can be presented by graphs as shown in Figure 4. The gelation (top left corner and magnification) is a key point in analysing the results, as it provide the time of gelation t_{gel}, which is marked on the time axis. The time of gelation t_{gel} is the indicator for the temperature of gelation T_{gel} and the degree of cure of gelation c_{gel}. T_{gel} and $c_g el$ are defined by eqs. (6a) and (6b). The temperature of gelation T_{gel} and the degree of cure of gelation are graphically shown in Figure 4 as the intersection between the dashed blue line indication the time of gelation t_{gel} and the temperature curve or degree of cure curve respectively. The temperature of gelation has is marked on the temperature axis in Figure 4 and the degree of cure of gelation is marked on the degree of cure axis in Figure 4. Another key point from the cure cycle results are the strain level at room temperature[1]. The strain at room temperature is found at the time during cool down where the temperature first reaches the defined room temperature as shown in Figure 4.

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[1]The room temperature are here taken to be 25°C.

Ulrich A. Mortensen, Tom L. Andersen, Jacob Christensen, Marco Aurelia Miranda Maduro

$$T_{gel} = T(t = t_{gel}) \tag{6a}$$
$$c_{gel} = c(t = t_{gel}) \tag{6b}$$

Figure 4: Measurements of Cure cycle D where the temperature is held (nearly) isothermal at 80 °C. The time of gelation t_{gel} are used to find the temperature of gelation T_{gel} and degree of cure of gelation c_{gel}. The (near) isothermal cure makes it possible to extract the post gelation chemical shrinkage ε_{Ch} and the thermal strain ε_{Th}. The total process induced strain ε_{tot} is given when the cool down temperature hits 25 °C.

Table 2: Summary of results.

Cure Name	Cure Type	$\mathbf{c}_{gel}$ Nominal [-]	$\mathbf{c}_{gel}$ Mean	$\mathbf{c}_{gel}$ Std.dev	$\mathbf{T}_{gel}$ [°C]	ε_{Ch} [%]	ε_{tot} @ 25 °C [%]
A[a]		0.927			80.3	N/A	-0.74
B	Two Step	0.702			34.7	N/A	-0.20
C		0.607	0.715[b]	0.112[b]	41.2	N/A	-0.17
			0.661[c]	0.045[c]			
D	One Step	0.642			85.5	-0.20	-0.71
E		0.695			117.8	-0.17	-0.95

[a] This cure cycle did not reach gelation during the low temperature stage of the cure. Gelation occurred during the end of the temperature ramp from 30 °C to 80 °C. The DEA signal for the cure cycle is not reliable.
[b] Incl. Cure A
[c] Ecxl. Cure A

Ulrich A. Mortensen, Tom L. Andersen, Jacob Christensen, Marco Aurelia Miranda Maduro

The one step cure cycles D and E both had temperature overshoots of the isothermal target temperature of 7 °C and 10 °C respectively. The overshoot for both is the results from high exothermic heat release during the relative high rate of curing attained for these high temperature cures. The heat dissipation of the experimental set up is not capable of dissipating enough heat to prevent some thermal overshoot. Considering other relevant experiments (e.g [1]), the thermal overshoot is within reasonable limits for simulating an isothermal cure cycle. Considering the thermal overshoots to only have small effects, the one step cures can be used to asses the level of chemical strain that is build up in the post-gelation epoxy as shown in Figure 4. The sum of chemical strain ε_{Ch} and the thermal strain ε_{Th} is defined to be the total process induced strain ε_{tot} as given in eq. (7). The full results of the total strain at room temperature ε_{tot}, chemical strain ε_{Ch}, temperature of gelation T_{gel} and degree of cure at gelation c_{gel} is printed in Table 2.
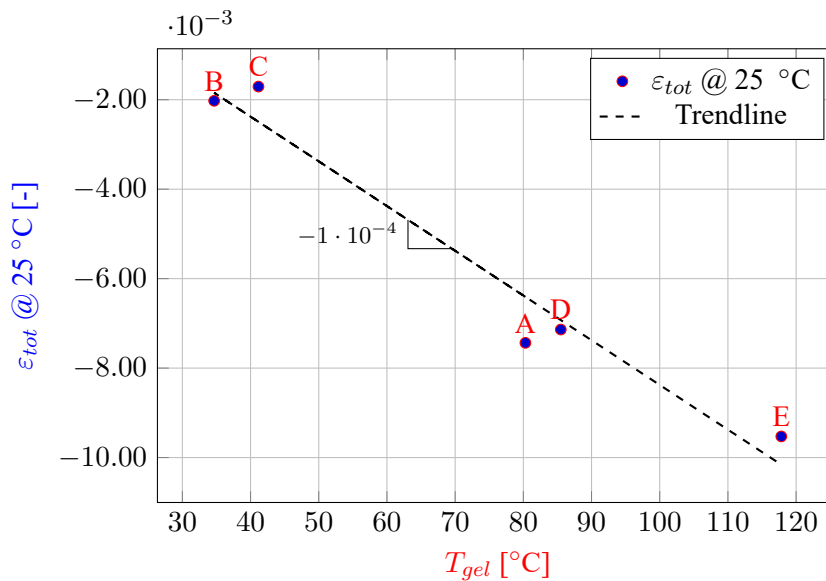
Figure 5: The total process induced strain ε_{tot} plotted against the temperature of gel T_{gel}.

$$\varepsilon_{tot} = \varepsilon_{Ch} + \varepsilon_{Th} \tag{7}$$

The total induced strain from processing have a negative correlation with the temperature of gelation. This relationship is in Figure 5. Cure A did not reach gel during the first low temperature step (30 °C) of the cure, which resulted in gelation at the high temperature step (80 °C) causing the total strain for the cure to resemble that of Cure D. While Cure A failed the purpose of causing low total induced strain, the resultant combination of T_{gel} and ε_{tot} at 25 °C closely fits that of Cure D. This gives indication that a two step cure is not effective unless the epoxy reaches the point of gelation during the low temperature step. The data point for Cure E in Figure 5 fits with the linear tendency between temperature of gelation and total process induced strain. This is even though a significant part of the cool down from 110 °C to room temperature occurred when the material was in a rubbery material state[2], where the coefficient of thermal expansion (CTE) is expected to be significantly different from the CTE in the glassy material state[3]

4 Conclusion

An experimental methodology was presented to the evaluate how the level of process induced strain in epoxy at room temperature is affected by the temperature profile used during cure. The methodology al-

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[2]$T > T_{glass}$, $T_{glass} \approx 80$ °C
[3]$T < T_{glass}$

Ulrich A. Mortensen, Tom L. Andersen, Jacob Christensen, Marco Aurelia Miranda Maduro

lows the resin to build up chemical and and thermal strains with insignificant influence from mechanical constraints. Three key values can be extracted from the experiments; The temperature of gelation T_{gel}, the degree of cure of gelation c_{gel} and the total induced strain at the room temperature (or other relevant temperature). These three key values can be used to design cure profiles that aims to lower the level of process induced strains and are likely to enhance the fatigue life properties of epoxies reinforced with non-crimp fabric glass fibre.

The results of the experiments indicates to the point of gelation, and especially the temperature of gelation, is likely to play a key role when for the the total process induced strain level in glass fibre reinforced epoxies.

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