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Effects of through-thickness dielectric sensor on carbon fibre epoxy cure monitoring

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ARTICLE INFO	A B S T R A C T		
<i>Keywords:</i> Thermosetting resin Cure behaviour Electrical properties Dielectric sensors	Dielectric sensors are an appealing solution for in-situ cure monitoring of thermoset polymers and thermoset composites. Analysis techniques have been shown to produce highly accurate and repeatable insight into cure state metrics both during and after cure. However, most dielectric sensors only report data on the surface of the material that the sensor is in direct contact with, neglecting the remainder of the thickness of the component. This study evaluates a novel dielectric sensor which is designed with a 20 mm penetration depth to monitor through the thickness of the composite part. While the prototype sensor design was shown to influence the raw data signal, a correction factor was successfully applied, and signals were analysed in accordance with the standard set of dielectric methods. The corrected signal had good accuracy and repeatability across laminates from 2 to 20 mm thick demonstrating a non-invasive through-thickness monitoring for a range of part designs.		

1. Introduction

Dielectric analysis is an increasingly attractive method for process monitoring of polymer and composite systems. Recently there has been considerable research on dielectric analysis for monitoring thermoset polymers and thermoset composites during both isothermal and dynamic cure cycles [1–4], such as for epoxies [5–9] and polyesters [3,8]. Dielectrics have also been used for crystallisation monitoring in thermoplastics processing [10-12], composite damage detection [13,14], evaluation of adhesive bonds [15], resin infusion flow [16-18], characterisation of residual stress [19-21], and prediction of resin state prior to infusion [22]. One of their most attractive capabilities is for in-line sensing of thermoset cure processes. Traditional temperature monitoring techniques use the time/temperature relationship for a thermoset polymer, which is dictated by cure kinetics reactions [23,24]. A major advantage of dielectric sensors is they can capture the molecular movement during cure, leading to identification of major curing events such as gel and vitrification [25,26]. Dielectric sensor cure monitoring capabilities and limitations have been well documented [27,28]. The sensing methodologies have been compared with known off-line analysis techniques [29,30] and other in-line monitoring sensors including ultrasonics and fibre optics [31-33].

Current trends towards live-monitoring and active control of the manufacturing process [34–37] rely on accurate, repeatable sensing

methods which capture cure progression through the entire part. Many techniques rely on sensor networks to monitor various locations throughout the part. Cure monitoring for very thick parts, such as up to 20 mm [24], has additional challenges, as surface or contact measurements are unlikely to be representative of the cure gradient existent through the part [38,39]. Use of invasive techniques such as embedded sensors [40] can capture through-thickness cure data, however the presence of the sensor in the cured part can compromise the mechanical performance of the final component. Dielectric cure monitoring can be comprised of different sensor configurations such as interdigitated electrodes, tool mounted monotrodes, or parallel plate electrodes. Interdigitated sensors and traditional monotrode sensors cast a narrow fringe field to take a contact measurement. Through-thickness dielectric monitoring is historically achieved using parallel plate electrodes [6,29]. However, this configuration is sensitive to part thickness changes during cure and results rely on correct alignment of the electrodes. To date, there are no commercially available sensors which can monitor through the thickness of large cross-sections without embedded sensors or a parallel plate configuration. This paper investigates a prototype monotrode sensor design, in which the electrode configuration creates a bulk field which is theoretically capable of measurements up to 20 mm. The bulk field is generated by the sensor housing, which functions as a negative electrode, and the inner positive electrode [41]. The electrode spacing controls the theoretical bulk field range, which for the

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Fig. 1. An equivalent circuit diagram depicting the response of the fibre bodies (purple, bottom), uninterrupted resin (teal, middle), and the layers of individual fibres within resin (green, top). Image is adapted from [41] Figure 5.18. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

sensor investigated in this paper is 20 mm.

Dielectric sensors apply an electric field which alternates in response to a set frequency or frequencies. The applied electric field causes a response from the charged particles within the material. For a reactive polymer, such as a thermoset, the electrical response of the material changes throughout the curing process [42]. The electrical response of mobile charges and dipoles become restricted as the material crosslinks and these charged particles become fixed in place. Within a given material there is a given concentration of ions, which are mobile charge carriers such as from impurities and unreacted monomer, and of dipoles. In addition to ions originating from impurities and monomers, considered extrinsic charge carriers, there is also a concentration of intrinsic charge motion due to the shifting of electrons in molecular bonds [43]. However, these bonds along the polymer chain do not drastically change during cure compared with the response of mobile ions and dipoles. Dipoles can be induced from charge separation within the polymer chain, or permanent dipoles which exist most commonly as mobile branches along the chain [43]. Ion mobility results in an electric current and strongly contributes to the conductive behaviour of the material. Dipole rotation and relaxation, or the storage and release of energy due to dipole alignment, causes capacitive behaviour. The overall dielectric response is dictated by the quantity and type of charge carriers and dipoles present in the material.

Dielectric behaviour in thermoset polymers can be modelled by an electric circuit, a diagram for which can be found in Fig. 1 which is adapted from [41]. This equivalent circuit diagram accounts for the

resistance of the carbon fibre body (R_{CP}) which forms a continuous conductive body which is in direct contact with the sensor. A layer of glass fibre is placed on top of the sensor to isolate the electrodes from the conductive carbon fibres, which for the purposes of this study is then considered to be a part of the dead body of the carbon fibre and thus represented by R_{CP} . As is documented in [41], in series with this is the undisturbed resin response formed from the parallel circuit containing a capacitor (C_P) and resistor (R_P). Lastly, we can find in series the influence of the mixture of individual carbon fibres (R_{SC}) and the resin response, combined with the blocking capacitance (C_{BC}) between the resin and individual fibres due to charge accumulation at the interface. Unlike in [41], Fig. 1 neglects the blocking capacitance at the sensorsample interface as this type of polarisation has been shown to be negligible in this study.

When the electric field is applied, the resulting excitation voltage (V)causes the material to respond with an applied current (I). This response comes after a delay called the phase shift (φ), which indicates how rapidly the material responds to the applied electric field. Based on this shift, the material responds with a capacitive (C) or conductive (G)response, which then drives the values of the measured dielectric signals [44]. This phenomenon, shown as the material admittance (Y) represented on the complex plane, is conveyed in Fig. 2. This is most represented as the material impedance (Z), as defined in Eq. (1). The real component of the material admittance is the bulk conductive response, which is represented in dielectric analysis as the ionic conductivity (σ). The imaginary component of the admittance gives the capacitive response, which provides the material permittivity (ε^*). The complex permittivity is comprised of a storage component (ε') and a loss component (ε'). It can also be represented as a ratio called the dissipation factor (D), or $tan\delta$, for which delta (δ) is the complementary angle to the phase shift. The calculations for these parameters can be found in Eq. (2) for the ion conductivity, (3) for the permittivity (ϵ'), (4) for the loss factor, and (5) for the dissipation factor. It is worth noting that the ionic conductivity can be represented as the inverse of the resistivity or ion viscosity (ρ). These equations use the scaling factor or shape factor (A/ *d*), permittivity of free space ($\varepsilon_0 = 8.854 \text{ x } 10^{-12} \text{F m}^{-1}$), and electrical excitation frequency (ω).

$$Z = \frac{1}{Y} = \frac{1}{G + i\omega C}$$
(1)

$$\sigma = \frac{1}{\rho} = \frac{G}{\left(\frac{A}{d}\right)}$$
(2)

$$\varepsilon' = \frac{C}{\varepsilon_0\left(\frac{A}{d}\right)} \tag{3}$$

$$\varepsilon'' = \frac{G}{\omega\left(\frac{\Lambda}{d}\right)\varepsilon_0} \tag{4}$$



Fig. 2. Demonstration of how phase shift is derived and the impact that it has on the dielectric capacitance (C) and conductance (G).



Fig. 3. Laminate schematic showing the configuration of (left) the DEA laminate and analytical sub laminates and (right) and exploded view showing the sequence of the sub laminates, filler prepreg, and release film placement.

$$D = \tan\delta = \frac{\varepsilon''}{\varepsilon} = \frac{G}{\omega C}$$
(5)

Thermoset cure is a time-dependent dielectric process, meaning the dielectric behaviour changes throughout the physical cure process. This is commonly represented in dielectric analysis by monitoring the signal across a timescale for a set frequency or across a frequency-domain at set times. Dielectric spectroscopy, achieved by frequency analysis, can provide information on the molecular dynamics and their changes throughout cure [25,26]. This is a common technique used when molecular motion, such as from dipole relaxation, is the dominating force which contributes to the material cure. Time-spectrum analysis monitors the thermodynamic phase transitions as they occur over time. It is more appropriate to use this type of analysis when charge migration phenomena such as ion mobility dominates the signal, producing a frequency-independent result. An analysis of a given material over a range of frequencies can indicate the frequency-dependence of the signal and can assist the user in deciding which analysis methodology is optimal. Choosing a reasonable frequency for measurement is still important for time-spectrum analysis. The relevant time scale for out-ofautoclave thermoset curing is on the magnitude of minutes, so a 1 Hz frequency may be sufficient. However, faster curing thermosets which cure on the scale of seconds to minutes [45] may benefit from higher frequency measurements.

The dielectric signal can be influenced by several factors which distract from the direct material response. Parasitic effects such as electrode polarisation and internal surface charge build-up can occur due to ion movement during processing. Electrode polarisation occurs when mobile charges accumulate on the electrode surface. The build-up of surface charges on internal surfaces, such as along reinforcing fibre interfaces or other impurities, is called Maxwell/Wagner/Sillar (MWS) polarisation. Polarisation effects are identified by a distortion in the loss factor at low frequencies. Both types of polarisations must commonly be accounted for to ensure the effects do not distort the actual material response, typically with a correction factor or improved design. New sensors may also be influenced by the sensor and cable design itself [41], the processing temperature [46–48], and the presence of conductive fibres which can cause polarisation or electrical short-circuiting [49,50]. Calibrations of the temperature signal may be necessary to ensure accurate corrections are applied [51]. It should be noted that dielectric cure analysis has been established for use with carbon fibre reinforced polymers, provided the sensor electrodes are insulated from the conductive fibres using a film or barrier to prevent short circuiting [17,18,52-55].

This paper evaluates a novel tool-mounted monotrode dielectric sensor which is capable of monitoring through the thickness of a 20 mm component due to the circumferential electrode design. In this study a

Table 1

Laminate definitions including ply count, layup sequence, and sub laminate terminology in which X indicates the part replicate. Sub laminates are indicated by the bottom (B), middle (M), and top (T) location. Fibreglass plies are designated by "FG" and release film locations are designated by "RF".

Laminate	Ply Count	Layup Sequence	Test Panels
TMM20- 1,2,3,4,5	144	FG, [0/90] _{4s} , RF, [0,90] ₂₄ , RF, [0/90] _{4s} , RF, [90,0] ₂₄ , RF, [0/	TMM20-XB, TMM20-XM, TMM20-XT
TMM15-1,2	100	$FG, [0/90]_{4s}, RF, [0,90]_{13}, RF, [0/90]_{4s}, RF, [90,0]_{13}, RF, [0/90]_{4s}, RF, [90,0]_{13}, RF, [0/$	TMM20-X1 TMM15-XB, TMM15-XM,
TMM10-1,2	66	90] _{4s} FG, [0/90] _{4s} , RF, [0,90] ₄ , 0, RF, [0/90] _{4s} , RF, 0, [90,0] ₄ , RF, [0/	TMM15-XT TMM10-XB, TMM10-XM,
TMM5-1,2	34	90] _{4s} FG, [0/90] _{4s} , RF, [90,90], RF, [0/	TMM10-XT TMM5-XB, TMM5-
TMM2-1,2	16	50] _{4s} [0/90] _{4s}	TMM2-XB

popular out-of-autoclave carbon fibre/epoxy prepreg was cured in thickness ranging from 2 mm to 20 mm, with repetitions of each thickness included to determine the consistency of the results. The results of the dielectric analysis were used to evaluate the sensor behaviour and capabilities. Firstly, the sensor characteristics are evaluated, including investigations on the influence of temperature, conductive carbon fibres, polarisation, and sensor configuration and design effects. Next, a correction factor is provided which accounts for the influence of part thickness and temperature on the dielectric response. Finally, a comprehensive evaluation of dielectric analysis methods is conducted on the corrected signal. Special attention is paid to the accuracy and repeatability of the signal in predicting the cure properties through the entirety of the component thickness.

2. Methods

2.1. Materials and sample preparation

This study used Solvay CYCOM® 5320–1/IM7 carbon fibre/epoxy prepreg [56] which was stacked to thicknesses of 2 to 20 mm. Five replicates of 20 mm laminates were fabricated, in addition to two replicates of each thickness 2-, 5-, 10-, and 15-mm. Laminates are designated by their thickness and replicate number, for example TMM20-3 is the third replicate of the 20 mm thickness. One half of each laminate measuring approximately 80 mm by 80 mm was dedicated to the dielectric sensor reading. The second half of each laminate, also measuring 80 mm by 80 mm, was dedicated to analytical testing. Due to the large thicknesses of some of the panels, the analytical half of the



Fig. 4. Layup configuration showing (a) the bagging schematic and orientation of the laminate on the tool, (b) the vacuum bagged laminate in the oven including the air thermocouple placement, and (c) the location of the sensor in the tool relative to the laminate sections.

laminate was separated into sub laminates using a release film. The film was used to separate each laminate into five segments: three testing panels located at the bottom, middle, and top of the laminate and two filler segments which are used to space out the testing panels to the appropriate thicknesses. A schematic of this is shown in Fig. 3. The testing panels each had the layup definition of $[0/90]_{4s}$ and the filler panels had the layup definition of $[0/90]_{4s}$ and the filler panels had the layup definition of $[0/90]_x$ where x is determined by the layup sequence. A ply of dry fibreglass was placed under the DEA half of the laminate to isolate the sensor from the conductive carbon fibres. Layup sequences and analytical sub laminate nomenclature is given in Table 1.

The parts were laid up on a 15 mm thick steel tool in which the NETZSCH through-thickness sensor was mounted. The sensor location relative to the tool and laminate is shown in Fig. 4(a) and (c). The laminate was then vacuum bagged in accordance with the manufacturers recommended vacuum bagging schematic [56], also replicated in Fig. 4(a). The parts were cured in an air circulating oven starting from ambient conditions. Fig. 4(b) shows the bagged laminate in the oven. The temperature was increased at a rate of 2 °C/min to 180 °C, followed by a 2-hour dwell at 180 °C as determined by the lagging thermocouple (bottom TC), before cooling to ambient temperatures. This modified version of the manufacturers recommended cure cycle was used for simplicity, as the single dwell temperature allows thermal effects on the sensor to be accounted for.

Data was collected by the dielectric sensor, which is mounted flush with the surface of the tool, and with embedded K-type thermocouples. Thermocouples (TC) were embedded within the DEA half of the laminate, with care taken to ensure that the thermocouples did not lie directly over top of the sensor location. They were embedded on top of the first ply (bottom TC), in the middle of the laminate (middle TC), and below the final ply (top TC). An additional thermocouple was placed approximately 100 mm above the surface of the laminate to measure the air temperature (air TC). The data collected from these panels follows the data flow in [57]. The following sections detail the methods used to complete the dielectric analysis, cure simulation, and analytical testing.

2.2. Dielectric analysis

2.2.1. Data collection

Dielectric data was collected using a prototype NETZSCH Tool Mounted Monotrode (TMM) sensor and the NETZSCH DEA 288 *Ionic* data analyser. The sensor is a prototype monotrode design with a circumferential electrode configuration, in which the electrodes were spaced by polyetheretherketone (PEEK) rings. The electrode design is based on the TMM10 sensor and is adapted to allow for both fringe electrical fields and bulk fields which arc up to 20 mm into the component. The choice of PEEK as the spacer material was selected due to limited material availability due to the COVID-19 pandemic and is not the material of choice for this sensor design. The influence of the PEEK is investigated in this paper to determine if there is similar behaviour to the substrate of an interdigitated sensor, in which the choice of material is known to influence the sensor functionality [58].

The sensor collected parameter data for frequencies between 1 Hz and 10 kHz with 4 frequencies set logarithmically per decade. The dielectric parameters under investigation in this paper are the dissipation factor (*D*, also known as $tan\delta$), impedance (*Z*), ion conductivity (σ), loss factor (ε "), and permittivity (ε "). In accordance with the authors previous study [57], logarithmic scaling was used for each parameter to isolate the impact of curing on the dielectric signal. Data was processed using NETZSCH Proteus® software, with the signals smoothed up to software setting 6–10 to minimise signal noise. The phase angle (φ) for each test was also recorded and used to evaluate the sensor functionality.

2.2.2. Sensor characterisation

Firstly, the performance of the prototype monotrode sensor used in this study was assessed. Dielectric sensors can be subject to a number of influences such as temperature [46,51], electrode and interfacial polarisation effects [1,59], and cable and sensor design [41]. Such effects can distort the signal and compromise measurements. As this sensor is a prototype these influences must be investigated.

Signal quality was evaluated using the phase angle and loss factor. The phase angle measurements were represented as a surface plot to evaluate the change of phase angle with time and across the frequency spectrum. The phase angle is expected to start at approximately 90 degrees at the beginning of cure, with a drop towards lower values due to the increase of material conductivity with the increased temperature. From the minimum phase angle, which roughly correlates to the point of minimum viscosity of the material, the phase angle increases back towards higher values as the curing reaction increases the material capacitance. The evaluation of this behaviour was used to validate the selected analysis frequencies and to verify the credibility of the

Table 2

Methods of identifying cure events through dielectric analysis (DEA) and RAVEN simulation. Adapted from [57].

Cure Event	DEA Identification Method	RAVEN Identification Method
Cure start	First local maximum of dX/dt	Onset of reaction rate increase
Minimum viscosity	Global maximum or minimum	Minimum of viscosity curve
Gel point Vitrification point	Endset after global max/min Tangent point after endset	Inflection of viscosity curve Crossover of T - T_g

measurement.

Polarisation effects due to electrode polarisation or interfacial polarisation were evaluated by reviewing the frequency spectra of the loss factor throughout the cure. The logarithm of the loss factor was plotted against the logarithm of the monitored frequencies for intervals of 10 min, and the slope was measured. A slope in the low-frequency region of -1 indicates a dominant Ohmic conductivity [43,60], and slopes which deviate from this indicate electrode polarisation. This analysis is presented for a selection of representative parts to identify if results are consistent across part thicknesses.

The impact of conductive carbon fibres, which may cause interfacial polarisation, was also tested. A previously cured sample, TMM20-2, was post-cured for 2 h at 200 °C to ensure completion of the cure reaction. The fully cured sample was then placed over the sensor, and vacuum bagged to maintain contact and location with the surface of the sensor and the tool. It was then processed through a standard cure cycle, and the dielectric signal analysed for drift. These results were compared with an empty test of the sensor in the tool, which was processed to the same temperature conditions but with no material present.

The sensor design, specifically the impact of the PEEK spacer rings, was also evaluated using an empty cure cycle. A dynamic cycle was run from 20 to 190 °C at a rate of 1 °C/minute, and dielectric spectra was evaluated to determine how the PEEK spacers may influence the sensor measurements. This temperature range was selected as it encompasses the T_g of PEEK, which is around 140 °C, and the maximum processing temperature for this study, approximately 180 °C. The loss factor was evaluated across the temperature domain for each frequency, and across the frequency domain at temperatures spaced at 10 °C increments. The relationship of loss factor to temperature demonstrated how the PEEK T_g impacts the dielectric signal, with the alpha relaxation event confirmed with the frequency domain evaluation.

2.2.3. Correction factor

As a result of the sensor characterisation, it was determined that a correction factor may be necessary to account for signal impacts due to the presence of the PEEK spacers. As a result of the PEEK in the design, the sensor is performing simultaneous readings of the PEEK and the curing epoxy. The PEEK causes a distortion of the signal which must be accounted for. However, the exact ratio of monitored responses is unknown, as it is dependent on the volume of material being tested and the electric field strength in that direction. As methods to evaluate field strength and direction were not available for this study, a correction factor was developed to account for the impact of the sensor design.

The primary assumption for the correction factor is that dielectric analysis has been proven to reliably and repeatably detect cure events for the material system under investigation [57]. To this end, a correction factor was determined by establishing a correlation between the DEA- and RAVEN-detected cure events, which are known to be reliably consistent with one another. The cure events were determined in accordance with Table 2 for each individual dielectric parameter. The cure end, as determined by the minimum of absolute value of dX/dt, was excluded from this analysis as the value is a direct response to the change in temperature experienced by the sensor. This value indicates the stopping of the cure reaction due to reduction in temperature and

Table 3

Dielectric anal	vsis methodology	v. Adapted from	[57]	١.
	,			

Name	Method	Relevant Publications
DoC (1)	$\alpha = \frac{\log X_0 - \log X}{\log X_0 - \log X_\infty} \alpha_{RAVEN}$ In which the X_0 is the	[2,29,73,74]
	maxima of the signal X , and X_{∞} is the end of the	
	isothermal region of the signal.	
DoC (2)	Linear regression of the log of the signal against	[4]
	the degree of cure calculated from the time of	
	global maxima to the end of the isothermal hold.	
Cure Start	First local maximum of dX/dt	[75]
Viscosity	Global maximum or minimum	[33,52,76]
Gel Point	Endset after global max/min	[33,52]
Vitrification	Tangent point after endset	[33,52]
Cure End	Minimum of absolute value of dX/dt	[54,75,77]

does not have an identifiable dielectric event associated with it and is therefore not necessary to correct for.

Individual Arrhenius plots were created for each part thickness to determine the impact of part thickness on the signal reading. The difference (Δ) between the time prediction from DEA and the time prediction from RAVEN was taken as $\Delta = t_{DEA} - t_{RAVEN}$. The natural logarithm of Δ was then plotted with the inverse of the temperature at the sensor, and a linear fit was applied according to Eq. (6). The fit parameters *m* and *b* for each part thickness were plotted against the part thickness to determine if there is a thickness dependence. The final parameters, with the incorporated thickness (*x*) dependences, were compiled into Eq. (7) to identify the correction factor which must be applied to the dielectric signal. In this equation the coefficient (*A*) is derived from the thickness dependence of *b*, and the exponential factor (*B*) is derived from the thickness dependence of *m*. The correction factor was subtracted from the time measurement for each dielectric function to produce a new, corrected time scale in accordance with Eq. (8).

$$\ln\Delta = m\left(\frac{1}{T}\right) + b \tag{6}$$

$$\Delta_{\text{correction}} = A(x) \exp\left(-\frac{B(x)}{T}\right)$$

Where $A(x) = \exp(b(x))$ (7)

and B(x) = m(x)

$$t_{\text{corrected}} = t_{\text{DEA}} - \Delta_{\text{correction}}$$
(8)

2.2.4. Cure analysis methods

The corrected dielectric signals are evaluated in accordance with the methods provided in Table 3, which is adapted from the methods evaluated in [57]. The degree of cure (DoC) methods utilises graphical techniques to plot the degree of cure progression. The remaining methods identify discrete cure events. All methods are compared for accuracy and repeatability against the RAVEN simulation data and the analytical results from DSC and DMA testing. For further details regarding the implementation of the analysis methods, the reader is directed to review [57].

To ensure consistency with the methods reported in [57] the 1 Hz frequency is used for all correlations excepting for the dissipation factor, which used a 100 Hz frequency. The dissipation factor at lower frequencies exhibited a double-peak behaviour which prohibited the definitions of Table 3 from being applied as described. The 100 Hz frequency demonstrated a shape which was reliably consistent with the remaining parameters. Rationale for this is presented in the sensor characterisation discussion regarding the phase angle.



Fig. 5. Phase angle in response to temperature and frequency for TMM20-2 (left) and TMM15-2 (right).

2.3. Validation of the dielectric analysis

2.3.1. RAVEN simulation

Convergent RAVEN software was used to simulate the cure of the prepreg based on the temperature profile collected through the thickness of the laminates. The simulation results were used to validate the result of the dielectric analysis. The bottom ply, mid ply and top ply thermocouple readings were input into a 0D temperature profile using the material card for CYCOM® 5320–1/IM7-12 K, which is based on the Kratz cure kinetics model [61]. Cure features were identified in accordance with the methodology from [57], in which publication the reader is suggested to review Fig. 3 for a visual depiction of cure event identification:

• The final degree of cure is identified as the end value of the degree of cure curve.



Fig. 6. Phase angle comparisons for 1 Hz and 100 Hz for TMM20-2 and TMM15-2.

- The vitrification point is identified as the crossover point between the T_g and temperature.
- The final T_g is identified as the end value of the T_g curve.
- The start of cure and end of cure is indicated by the start and ending of the cure reaction rate.
- The time at minimum viscosity is indicated by the global minimum.
- The gel point is indicated by the inflection of the viscosity curve.

As the dielectric signal collects a single measurement representing the full part thickness, the average of the three RAVEN measurements was considered. The analysis in this paper assumes that the sensor takes an equal reading through the entirety of the thickness, rather than a signal which is weighted towards or away from the surface of the sensor.

2.3.2. DSC and DMA

Prior to conducting analytical tests, the laminates were separated into the assigned sub laminates. The analytical half of the panel was cut from the DEA half of the panel, and the release coated film was used to separate the vertical stack of panels. From each part thickness sub laminates were extracted from the bottom, middle, and top of the laminate (designated B, M and T), and the filler sections were discarded. It should be noted that due to part thickness limitations the 5 mm laminate was only comprised of a bottom and a top sub laminate, and the 2 mm laminate was only comprised of a bottom sub laminate.

Differential Scanning Calorimetry (DSC) was conducted using a TA DSC25. Approximately 5–10 mg of material cut from each sub laminate, and was tested under a dynamic ramp rate of 5 °C/min from 25 to 280 °C. The actual laminate degree of cure was calculated by integrating under the heat flow-time curve and dividing by the total heat of reaction for 5320–1, which is indicated as 561.8 J/g per Convergent RAVEN.

Dynamic Mechanical Analysis (DMA) was conducted using a TA HR-2 Hybrid Rheometer. Test coupons were cut by waterjet from each sub laminate to dimensions of 8 mm wide by 45 mm long with a tolerance of \pm 2 mm. They were dried in an air circulated oven at 120 °C for a minimum of 16 h, and then held in a sealed container with desiccant prior to testing. Coupons were tested by a dynamic ramp rate of 5 °C/ min from 25 to 280 °C with a displacement of 50 µm oscillating at 1 Hz frequency. The T_g was calculated in accordance with ASTM D 7028 [62] by the storage modulus (*E*') onset, and the degree of cure was calculated using this value and the DiBenedetto equation.



Fig. 7. Frequency spectra of the loss factor for TMM20-2, TMM10-1, and TMM2-1 to investigate the presence of electrode polarisation.

3. Processed TMM sensor results

3.1. Sensor characterisation

3.1.1. Phase angle

The phase angle response provides information on the ratio of the conductive and capacitive behaviour of the material. This can be used to evaluate the credibility of the signal measurement and to identify potential erroneous signal responses. Phase angle measurements over time and across the frequency spectrum was compared for TMM20-2 and TMM15-2, which are representative of the two responses seen in this study. A surface plot of the entire frequency spectra is shown in Fig. 5 for these two tests.

In general, the phase angle measurements from all part replicates display the expected behaviour, which validates the measurements taken for this study. Both signals drop initially, indicating an increase in conductive behaviour, which is the expected response due to the increase in temperature allowing for an increase in mobility of conductive charges. TMM20-2 shows an increasing phase angle after the point of maximum conductivity, which occurs at 99 min for the 1 Hz measurement. This corresponds to the increasing capacitive behaviour due to the progression of the cure reaction which restricts ion and dipole mobility. However, TMM15-2 shows a double peak behaviour around the minimum phase angle for low frequency measurements. This is due to a very high magnitude of loss factor for this measurement. The double peak behaviour disappears in frequencies higher than 100 Hz, with Fig. 6 showing the individual measurements at 1 Hz and 100 Hz for these two parts. Qualitatively, the 1 Hz and 100 Hz signals for TMM20-2 show similar responses, just of differing magnitude. Due to the double peak behaviour for some parts at low frequencies, the 100 Hz measurement was selected for the dissipation factor analyses, as the dissipation factor is directly calculated from the phase angle. Using the 100 Hz measurement ensures that the definitions used in the analysis methodologies can be applied. However, the 1 Hz measurement is applicable to the remaining parameters, as they are not impacted by the inversion of the phase angle.

3.1.2. Polarisation effects

Electrode polarisation due to build-up of charges on the electrode surface is a known concern for dielectric sensors. Polarisation due to interfacial charge build-up, called Maxwell/Wagner/Sillar (MWS) polarisation, is also common in dielectric monitoring of multi-phase materials. In the case of a carbon fibre reinforced epoxy, the interface between the carbon fibres and the epoxy is where the charges are likely to build up. Three representative tests were evaluated through the frequency spectrum to further understand potential polarisation effects. TMM20-2, 10–1 and 2–1 were selected as representative tests to evaluate polarisation for the range of part thicknesses. The samples were



Fig. 8. Results of the sensor drift test (labelled Empty Cure) and the conductive fibre test (labelled Fully Cured) in comparison with TMM20-2 cure test.

plotted against the measurement frequencies to evaluate the slope on a log–log plot. Measurements with a slope of -1 are known to follow Ohm's law and indicate the measurement is conductivity-driven and free from polarisation effects. The three sets of curves, shown in Fig. 7, show that the samples are free of obvious polarisation effects. All measurements display a slope of approximately -1 at lower frequencies and display no notable deviations or erratic behaviour which would indicate polarisation. From this it is concluded that either this sensor is free of MWS polarisation effects, or that the effects are significantly minor in comparison with the cure signal. A deeper investigation into frequency effects and relaxation events will be provided in the following section.

It is also possible that the presence of the conductive carbon fibres can influence the signal due to polarisation at the interface with the matrix. Dielectric measurements were collected for tests with no curing reaction present to isolate the influence of the carbon fibres. The sensor was tested with an empty set up, without the presence of any prepreg material, to determine the impact of temperature on the sensor reading. It was then tested with a fully cured sample (TMM20-2) which was postcured to 100 % conversion, to identify the impact of the presence of conductive fibres. The ion conductivity of the empty test and the fully cured tests are given in Fig. 8 and compared with the original dielectric signal for the TMM20-2 cure for reference. It is apparent that there is a slight sensor drift over time as the temperature increases, which will be discussed further in the following section. The conductivity measurement of the fully cured sample is very slightly higher than the empty test.



Fig. 9. Loss factor measurements for PEEK integrated into the sensor showing (top) frequency domain response and (bottom) temperature domain response.

This can be attributed to the lingering conductivity in the cured sample, for example intrinsic conductivity from electron shifts in atomic bonds. Overall, the response of the fully cured signal aligns with the response of the sensor itself to temperature effects which will be explored in more detail in the next section. There are no notable effects from the presence of the carbon fibre which need to be accounted for in these tests. As the carbon fibre reinforcement itself is not changing during the cure process, the relative change in dielectric signal which is observed during the part cure is attributed only to the epoxy cure reaction. This study is specifically concerned with the relative change in the dielectric signal as a way of evaluating material change. This is in contrast with other applications of dielectric materials which may use the magnitude of the dielectric signal to assess material properties. For this reason, the slight change in

signal magnitude due to the carbon fibres can be disregarded.

3.1.3. Impact of PEEK

As can be seen from the comparison Fig. 8 the sensor itself displays a response with temperature. This is attributed to the simultaneous measurement of the epoxy-based prepreg which is being cured, and the measurement of the PEEK rings which are spaced between the electrodes. The melting and softening temperature of PEEK is dependent on the specific composition and relates to the molecular weight and crystalline content. In general, PEEK has a melting point between 330 and 340 °C, depending on the content of the crystalline and amorphous phases [63,64]. The rubbery region, again depending on the polymer blend, can begin in the region of 240 °C [65]. As temperatures in this



Fig. 10. Loss factor measurements for (top) PEEK compared with (bottom) TMM20-2 measurement including PEEK and epoxy components.

study do not exceed 180 °C, it can be concluded that the PEEK does not approach its melting range or softening point. Instead, the critical transition is the glass transition which for PEEK exists around 140 °C [66,67]. There have been several dielectric spectroscopy evaluations of PEEK relating to the alpha relaxation events, which are representative of the glass transition. Studies have shown that alpha relaxation is sensitive to the crystalline content of the polymer [68], with the amorphous material mobilising at temperatures above the glass transition [69]. The presence of the crystalline region can cause a broader relaxation range compared with the amorphous material [70], with previous studies showing a sharp increase in the dielectric loss for the amorphous phase at a range of frequencies [69]. In the time-domain, the amorphous and crystalline phases cause an increase in the dielectric loss and permittivity in response to the glass transition [71].

The results of the loss factor for the dynamic temperature test of the sensor are given in Fig. 9. The results display the same trends documented in the literature: notably the visible increase in loss factor is clear once the temperature exceeds 140 °C. The increase in loss is less prevalent for higher frequency measurements, however the molecular mobility is visible across the frequency spectrum. Also clear are molecular relaxation events at 31.6 Hz and 100 Hz. The presence of two relaxation peaks may be a result of the limited frequencies evaluated in this range for this test, or it may be indicative of individual relaxation peaks for the amorphous component of PEEK and crystalline component of PEEK. Regardless of the original processing conditions of the PEEK during the manufacture of the sensor, it is likely that the material has



Fig. 11. Application of (a) an electric field (*E*) to a multi-phase material and (b) two individual measurements by two individual electric fields for which $E = E_1 + E_2$ onto two individual materials, as is applicable in this study.

fully crystallised during the heating and cooling during the sensor trials. Therefore, the 31.6 Hz peak may be attributed to the mobile amorphous phase, as this peak becomes clearly visible only once the glass transition has been reached. The 100 Hz peak is visible through the entirety of the temperature range and may be attributed to the more restricted crystalline phase.

This response is also clear in the epoxy measurements for this test, during which a simultaneous epoxy-PEEK measurement is taken. Fig. 10 compares PEEK and epoxy-PEEK measurements, showing similar relaxation events at 31.6 Hz and 100 Hz. The presence of these peaks in later durations of the cure indicates that in the early stages, when the epoxy has the highest mobility, the epoxy response dominates the dielectric signal. The magnitude of the values for the PEEK are lower than those as measured in the epoxy tests, however, this is not necessarily indicative of the measurement ratio.

Dielectric measurements of multi-phase materials have been represented by the simple mixture bounds demonstrated by Eq. (9) [70]. However, these are thought to be overly simplistic, considering only the volume fraction of each material. An array of assumptions regarding morphology, isotropy, and geometry have allowed for development of complex permittivity bounds for a material with three or more components [72]. However, both calculations are based on the chief assumption of homogeneity of the material in which both materials are exposed to the same electric field, which is not applicable here. The schematic shown in Fig. 11 conveys these assumptions. In (a) is a multi-phase material with known volume fractions of each component, and a known electric field (E) applied to a region of the material defined by a circle of radius r. For this case, regardless of the value of r the ratio of the material volumes remains the same. However, in (b) which is representative of the configuration in this study, we see that the two separate materials under test are impacted by separate electric fields of differing

strengths. Further, while the PEEK rings (impacted by E_2 radial fields) occupy a known volume, the quantity of the epoxy (impacted by E_1 bulk and fringe fields) is unknown. The material thickness, which is varied in this study, is quantifiable, however the radius of the impacted region is unknown. For this reason, it is impractical to assume the correct ratio of signal measurements for these tests.

$$\frac{1}{\frac{V_1}{\varepsilon_1} + \frac{V_2}{\varepsilon_2}} \le \varepsilon^* \le V_1 \varepsilon_1 + V_2 \varepsilon_2 \tag{9}$$

3.2. Temperature correction factor

A temperature correction factor was determined to account for the impact of the PEEK on the signal measurement of the epoxy. The correction factor was established by identifying the time shift between the sensor reading and the known material state, which was defined by RAVEN.

Firstly, the cure events were determined from both the dielectric signals and the RAVEN simulation in accordance with Table 2. The discrepancy strength (Δ %) for each pair was calculated in accordance with Eq. (10) and the average values for each part thickness and for individual parameters is represented in Fig. 12, The discrepancy strength is calculated from time differential between when the average RAVEN cure event occurs (t_{RAVEN}) and when the dielectric graph feature occurs (t_{DEA}) and then normalised by the overall cure time (t_{TOTAL}).

$$\Delta\% = \left| 100^* \frac{(t_{RAVEN} - t_{DEA})}{t_{TOTAL}} \right|$$
(10)

From Fig. 12 we can determine that there are two consistent trends of the discrepancy strength: the strength weakens (meaning the



Fig. 12. Discrepancy strength showing the initial difference between the dielectric signal and the simulated values for varying cure events. Shown as a function of the (left) part thickness and (right) dielectric parameter.



Fig. 13. Temperature correlations for each part thickness, indicating the fitting equation and R² for each part thickness.



Fig. 14. Discrepancy strengths for the corrected dielectric signal shown as a function of the part thickness (left) and dielectric parameter (right). Note that the y-axis scale is consistent with the scale reported in Fig. 11.

discrepancy value is higher) as the part thickness increases, and the strength weakens as the duration in cure progresses. As the temperature increases throughout the duration of the cure, it is indicated that there is a temperature dependence component to the discrepancy strength. These trends are consistent with the impact of PEEK on the signal reading: the signal is influenced by the temperature relative to the PEEK $T_{\rm g}$, and by the part thickness and therefore volumetric ratio of epoxy to PEEK. The other item of note is that within each dielectric parameter there is no identifiable trend, and thus we can conclude that the parameters are reasonably interchangeable. Based on this rationale, the next stages of the analysis make use of an averaged value across all parameters.

Molecular relaxation events in PEEK are known to follow Arrhenius trends [67,71], so this approach was used here. The temperature correlation plots are shown in Fig. 13, including the preliminary fitting equations and the R^2 indicating the goodness of fit for each function. From these equations, a master equation was derived to describe the behaviour of the entire system. The master equation fits the form of Eq. (7) with the thickness dependent functions indicated in Eqs. (11) and (12). It is worth noting the consistent trends with thickness for both the coefficient of the linear fit and the y-intercept. This indicates that the

signal correction must incorporate a thickness dependence, which is supported by the visible trend in the left figure of Fig. 12. Further, the correction factor corrects for the influence of PEEK on the dielectric signal and must account for the difference in material volume ratios between the sensor and the differing part thicknesses. The relationships derived in Eqs. (11) and (12) are the best function fit to account for this thickness dependence. Recalculations of the dielectric signal for all the tested thicknesses validates the goodness of fit of this set of correction functions and allow a simple correction of the signal.

$$A(x) = -224\ln(x) + 783 \tag{11}$$

$$B(x) = 135\ln(x) - 674 \tag{12}$$

The correction factor, Eq. (8), was applied to the signals and the cure event timing was recalculated. The new discrepancy strengths for the corrected signals are shown in Fig. 14. The corrected signals produce an extremely good fit to the predicted values of the different cure events. Compared with the initial discrepancy strengths, which reach as high as 10–14 %, the cure predictions in Fig. 14 are now all within 5 %. This is consistent with the accuracy seen in the IDEX sensors [57]. Further, the application of the correction factor appears to significantly reduce the



Fig. 15. Comparison of DoC(1) for the corrected and uncorrected ion conductivity signal for part replicate TMM20-1.

impact of part thickness. The corrected values also lack a strong preference for the dielectric parameter; thus, all parameters can continue to be used interchangeably. The point of minimum viscosity, which occurs around 145 °C, displays the closest fit. As this is the closest event to the onset of the PEEK T_g , which indicates the correction factor successfully accounts for the influence of the PEEK on the signal.

4. Dielectric cure analysis results and discussion

4.1. Graphical methods

Each part replicate and each parameter were evaluated for DoC(1) in accordance with the equation provided in Table 3. The curves were normalised by the average degree of cure determined by RAVEN and then compared with the average of the RAVEN degree of cure simulation curves. Firstly, the results of DoC(1) analysis on a corrected and uncorrected ion conductivity signal are given in Fig. 15. This comparison confirms the use of the corrected signal for this analysis, as the onset of the degree of cure increase is far more comparable to the RAVEN simulation. The uncorrected signal has an approximated 20-minute delay for the onset of the degree of cure increase. While the correct signal has a quicker rise to the full cure value compared to RAVEN, the general progression of the cure is aligned. The discrepancy can be attributed to the influence of PEEK on the signal magnitude. The results of DoC(1) for each parameter in each part thickness are given in Fig. 16. The remaining parameters and part thicknesses display a similar trend to Fig. 15: the onset of the cure reaction is accurate, and the general shape of the cure progression is aligned to that of the simulation. DoC(1) is shown to have good repeatability regardless of the part thickness or dielectric parameter used.

The results of DoC(2) for a representative part of each thickness, and for each dielectric parameter, are given in Fig. 17. The predicted final values of degree of cure for this method are given in Table 4. In general, the dielectric parameters estimate the average degree of cure progression with reasonable accuracy, and the parameters can be used interchangeably. The applied correction factor successfully shifts the time scale of the dielectric parameters, and the result aligns extremely well with the onset of degree of cure predicted by RAVEN. The general shape of the degree of cure curves matches well with that provided by RAVEN, with the conductivity-driven parameters, the ionic conductivity and loss factor, fitting slightly better to the degree of cure progression for cures between 50 and 80 %. In accordance with the methods in Table 3, the



Fig. 16. DoC(1) method applied to each dielectric parameter for each part thickness. Measurements are at 1 Hz excepting the dissipation factor which was measured at 100 Hz.



Fig. 17. DoC(2) method applied to each dielectric parameter for each part thickness. Measurements are at 1 Hz excepting the dissipation factor which was measured at 100 Hz.

Table 4

Predicted degree of cure values from DoC(2). Results are compared with analytical results from DSC and DMA and simulated results from RAVEN. DoC(2) value is averaged over all dielectric parameters. Analytical and simulated results are averaged over all replicates and part thicknesses.

Part	DoC(2)	DSC	DMA*	RAVEN
TMM20-1	90.0 %	94.9 %	95.5 %	95.2 %
TMM20-2	90.6 %	94.8 %	95.4 %	95.1 %
TMM20-3	89.4 %	94.6 %	95.5 %	94.7 %
TMM20-4	89.8 %	94.6 %	95.4 %	94.9 %
TMM20-5	90.7 %	94.4 %	95.0 %	94.4 %
TMM15-1	88.7 %	94.7 %	95.3 %	94.8 %
TMM15-2	88.9 %	94.5 %	95.4 %	94.9 %
TMM10-1	87.1 %	95.0 %	95.3 %	93.9 %
TMM10-2	77.1 %	94.6 %	95.6 %	94.0 %
TMM5-1	88.4 %	94.5 %	95.3 %	94.3 %
TMM5-2	89.0 %	94.7 %	95.1 %	93.9 %
TMM2-1	88.7 %	94.6 %	94.0 %	94.9 %
TMM2-2	87.8 %	93.6 %	93.8 %	93.9 %

* As calculated using the DiBenedetto equation.

predictions stop at the end of the isothermal temperature region, which occurs at 250 min. However, the actual predicted degree of cure progression continues until approximately 270 min. Due to this, the estimates do not capture the final stages of the degree of cure progression, and the final predicted values in Table 4 are slightly lower than the actual expected degree of cure. As with DoC(1) this method had reasonable accuracy for the corrected dielectric signal.

4.2. Cure point methods

In addition to the comparison provided in Fig. 14, comparing of cure point identification for the corrected dielectric signal with the RAVEN simulation is provided in Table 5. Included are the average value and standard deviation across all dielectric parameters and part replicates for each part thickness. Also shown is the average percent discrepancy

Table 5

Results of the corrected cure point analysis methods conveying the average time
at each cure event for each part thickness, the standard deviation, and the
percent discrepancy compared with the RAVEN simulation.

Cure Event	Part Thickness (mm)	Average Value (min)	Std. Dev (min)	$\Delta\%$
Cure Start	20	57.6	6.0	1.7 %
	15	57.1	5.0	1.7 %
	10	59.5	7.7	2.4 %
	5	55.5	3.4	1.0 %
	2	53.9	5.4	1.6 %
Minimum	20	86.8	1.1	0.4 %
Viscosity	15	85.6	0.2	0.5 %
	10	86.9	0.5	0.7 %
	5	86.1	0.5	0.8 %
	2	86.4	0.8	0.6 %
Gel Point	20	120.1	7.9	3.3 %
	15	122.2	8.2	4.0 %
	10	115.1	5.6	1.8 %
	5	119.9	5.5	1.9 %
	2	120.6	8.4	3.2 %
Vitrification Point	20	154.7	7.1	4.7 %
	15	153.7	5.4	2.8 %
	10	152.0	2.8	1.9 %
	5	154.2	5.6	1.6 %
	2	159.0	6.0	3.0 %
Cure End	20	251.6	4.0	3.0 %
	15	250.5	3.7	4.2 %
	10	247.9	6.3	3.0 %
	5	248.8	3.8	2.6 %
	2	251.5	2.4	2.9 %

calculated from Eq. (10).

5. Conclusion

A prototype dielectric sensor was evaluated in this paper for sensor

quality, applicability of analysis methods to through-thickness sensing, and part-to-part consistency. It was demonstrated that:

- Phase angle measurements and dielectric signals are reliable and as expected for the 5320–1 carbon fibre/epoxy material system.
- The sensor is free of polarisation effects, temperature effects, and the dielectric signal is not influenced by conductive carbon fibres.
- The presence of PEEK spacer rings in the sensor distorts the signal due to the simultaneous epoxy-PEEK reading and necessitated a correction factor. The correction factor assumes that the sensor identifies cure events in the same manner as the IDEX sensor, and accounts for temperature and thickness variation.

The application of the correction factor allowed for successful application of parameter-independent dielectric analysis methods. The corrected signal is very accurate and resulted in identifying cure point times within 5 % compared with averaged RAVEN results, including predicting the point of minimum viscosity within 1 % and the gel point within 4 %. Graphical methods were also applied with good accuracy, including degree of cure predictions from DoC(2) within 6 % compared to simulated and analytical methods. The averaged progression of cure was successfully monitored throughout the entire part thickness and applicable to parts from 2 to 20 mm thick. Finally, the results were repeatable for each part thickness across the manufactured replicates, indicating robustness of the sensor design.

CRediT authorship contribution statement

Molly Hall: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. Xuesen Zeng: Writing – review & editing, Supervision, Funding acquisition. Tristan Shelley: Writing – review & editing, Supervision. Peter Schubel: Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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