

**CURE MONITORING
TECHNIQUES FOR
POLYMER
COMPOSITES,
ADHESIVES AND
COATINGS**

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Measurement Good Practice Guide No 75

GOOD PRACTICE GUIDE TO CURE MONITORING

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Abstract

This Measurement Good Practice Guide covers real-time, on-line cure monitoring in the industrial processing of thermosetting polymer-based materials, such as fibre-reinforced composites, adhesives and coatings.

The Guide focuses on the five most commercially well-developed cure monitoring techniques: thermal, ultrasonic, acoustic, dielectric and strain sensing. The procedure, theory and analysis for each measurement technique is described in detail and their respective sensitivities to important stages during cure processing discussed. Typical examples of obtainable results are demonstrated using laboratory investigations, with supporting evidence of their application to real environments, processes and problems being provided by three industrial case studies. Recommendations are made on the choice of technique and important considerations when making an appropriate selection. Finally, the overall benefits of adopting cure monitoring are highlighted. The Guide provides a consolidated source of information to help exploit cure monitoring technology.

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GOOD PRACTICE GUIDE TO CURE MONITORING

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1 Scope

This guide describes cure monitoring methods relevant to the processing of thermosetting polymers used in adhesives, fibre reinforced composites and coatings.

Guidance for the selection of the most suitable technique is provided as well as procedures for conducting measurements for some of the most common and commercially available techniques. Techniques are compared based on their material/process suitability, cost, difficulty of application, sensitivity to relevant processing parameters etc.

Case studies included subsequently show examples of the application of some of the techniques as applied to typical industrial environments and materials.

2 Introduction

2.1 What is cure?

Cure is a process which converts a liquid mixture into a solid. This may be by means of a physical process or more usually by means of a chemical reaction. This basic process is shown schematically in Figure 2.1.

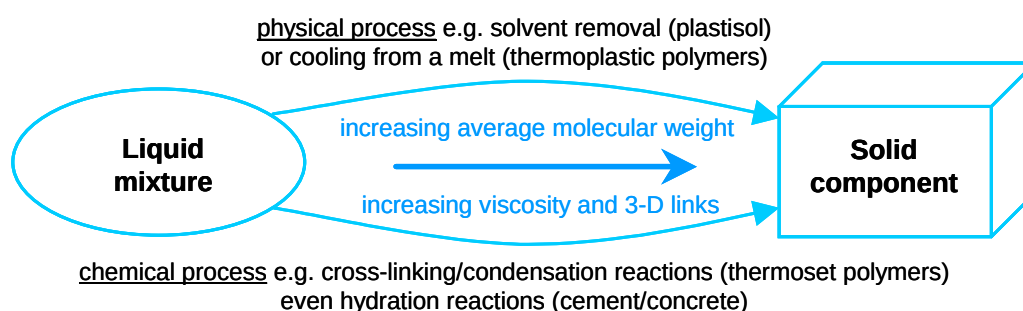


Figure 2.1 - Fundamentals of the process of cure.

There is a diverse range of materials which undergo cure, of which the following are just a few examples:

- epoxies
- poly or vinyl esters
- phenolics
- natural, synthetic, vulcanised or silicone rubbers
- polyurethanes
- acrylics
- cyanoacrylates
- polyimides
- concrete, cement or mortar.

The cure of thermoset polymers is a process that converts a liquid mixture of resin (polymeric precursors), catalysts, activators etc, into a solid by means of chemical reactions which are often activated by heat.

As cure progresses, there is an increase in molecular weight accompanied by an increase in viscosity. This continues until eventually the system reaches

“gelation” and is no longer able to flow. An increase in the number and density of 3-D structural cross-links follows until finally the material achieves “vitrification” [1]. At this point the material is usually a hard, glassy solid with a glass transition temperature higher than the cure temperature and no further cure reaction can be achieved at the chosen cure temperature. This marks the “end of cure”. At this point a particular “degree of cure” has been achieved, defined as the percentage of unreacted species conversion as compared to a “fully cured” material. A fully cured material has undergone as much reaction as possible such that further temperature increases or cure duration will not achieve further reaction.

Continued heating once vitrification has occurred may result in “degradation” of the cured solid with a reduction in cross-links and a corresponding loss in performance.

Alternatively, a secondary higher temperature “post-cure” heating stage is sometimes used to increase the glass transition temperature (T_g) and cross-linking, whilst avoiding the problems with volatiles and exotherms associated with high initial temperatures. In extreme cases this can lead to undercured and degraded material within the same component.

The series of events, typical of the progression of a cure reaction, is shown in Figure 2.2.

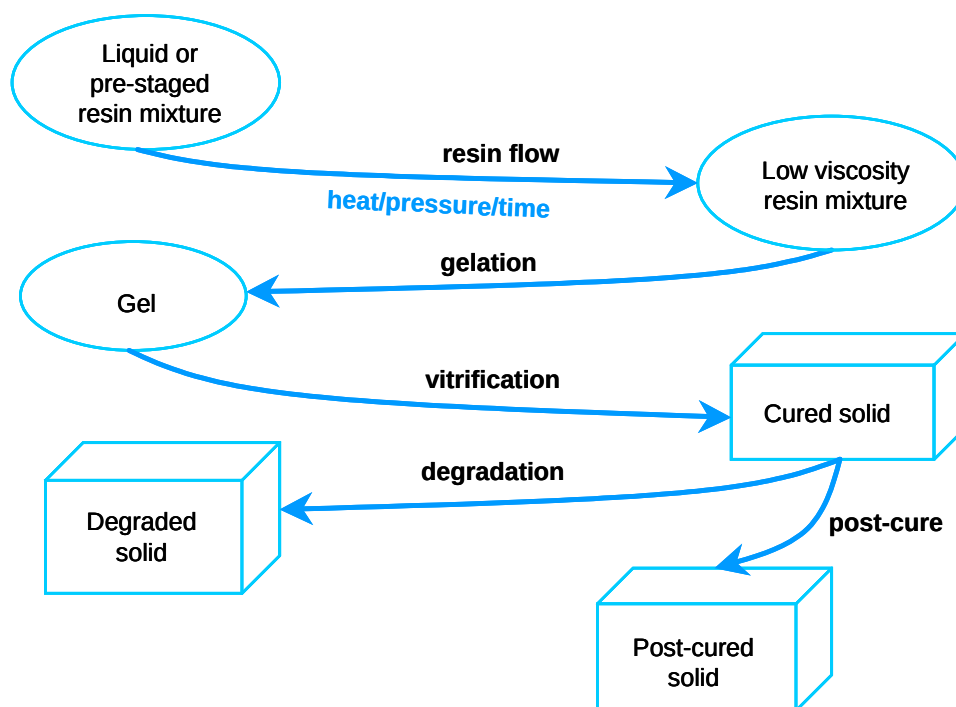


Figure 2.2 - Schematic of basic phase transitions identifiable using cure monitoring.

There is as diverse a collection of cure manufacturing processes as there are curing materials, each with distinct environmental conditions, tooling requirements and part access, involving either discrete or continuous part production. A small selection is listed below:

- filament winding
- pultruding
- hand lay-up/moulding
- press moulding
- resin transfer moulding
- injection moulding
- autoclaving
- “paint/bond and bake”.

2.2 What is cure monitoring?

Cure monitoring is a means of tracking the real-time changes in physical state or chemical reaction that occur during the curing process. “Real-time”

indicates measurements being carried out on a timescale which allows process conditions to be modified before completion.

These measurements are made with respect to cure time, in one of two ways:

- on-line -
 - ♦ on a single product or production line,
 - ♦ in-situ,
 - ♦ continuously,
 - ♦ sensors integrated into production process;
- or:
- in-line -
 - ♦ on multiple products or production line samples,
 - ♦ outside the production process,
 - ♦ at several discrete stages in parallel with production,
 - ♦ sensors are not integrated.

Cure monitoring enables several important transition stages or critical points during cure to be detected and identified, including:

- resin flow/position of flow front
- minimum viscosity
- gelation
- vitrification
- post-cure
- degradation
- degree of cure.

These characteristic cure stages help streamline processes in several ways. As the resin spreads, following the flow front ensures adequate mould filling and good fibre impregnation for reinforced materials. Once minimum viscosity is reached, often pressure is applied to reduce porosity and effect good consolidation of the material. This is frequently simultaneous to the removal of vacuum so the fluid resin is not flushed out of the part. Once gelation is achieved no more flow is possible and continued application of pressure achieves no further consolidation and so can be removed. At

vitrification, no more cure is attained at the defined processing temperature and so the part can be removed from the process and allowed to cool down. Alternatively, monitoring for the initial signs of degradation can be used as a trigger for part removal. Solid cured parts can then be collected and given a post-cure heat treatment together. The final measured degree of cure can then be used to ensure the part meets the specifications and requirements of the application.

2.3 Why monitor cure?

Despite the commonplace usage of polymer composites, adhesives and coatings in the manufacture of a seemingly limitless range of products; in fact very little has changed in the way these materials are processed from liquid resins into the finished component since mass production began.

Currently, a “black box” approach is used:

- processing is based on a rigorous compliance to the supplier’s recommended schedule
- assumptions are made about the material state
- time schedules are conservative.

Thus a rigid set of processing conditions (temperature and pressure) is adhered to, based on assumed material behaviour before, during and after cure, where conservative cure times are used which include safety and quality considerations. This allows no flexibility where different temperatures or pressures may be desired, or where material has aged differently or where safety margins can be narrowed. As a result, cure is a major proportion of both manufacture time and cost and the process is less efficient than it could be.

Issues which may need to be addressed include:

- deviations from supplier’s recommended schedule
- cure under uncontrollable ambient conditions
- variations in temperature and thickness across a component
- batch-to-batch variability in material
- effects of shelf-ageing or re-lifeing of material
- post-cure

- process line equilibration at start of working day
- occasional process line faults
- introduction of new formulations
- introduction of new processes.

Cure monitoring removes some of the uncertainties associated with these factors by assessing the state of the material, either directly or indirectly, as changes occur and allows appropriate adjustments and corrections to be made to ensure consistent properties and performance of the finished component. This results in optimisation of both the process and overall efficiency.

2.4 How is cure monitored?

Cure monitoring requires the measurement of a selected material property in order to assess the level of cure. Usually a greater change in the measured property indicates a higher level of cure.

The techniques can be grouped according to the material properties which are measured as a guide to the state of cure [2]:

- thermal -
 - ♦ temperature
 - ♦ thermal conductivity
 - ♦ thermal flux
- mechanical -
 - ♦ ultrasonic wave propagation
 - ♦ acoustic resonance
 - ♦ fibre optic strain sensing of cure shrinkage
 - ♦ piezoelectric sensor impedance
- electrical -
 - ♦ dielectric permittivity
 - ♦ conductive grid
- optical -
 - ♦ refractive index
 - ♦ spectroscopy (FTIR, Raman).

The implementation of the cure monitoring techniques will be discussed further; with emphasis being placed on the five most commercially available and industrially relevant methods, namely:

- temperature
- acoustic
- ultrasonic
- dielectric
- fibre optic strain sensing.

Practical examples and industrial application case studies based on these methods are also presented.

In addition to these techniques, more traditional methods ([3] which are not covered here) such as mechanical/hardness testing, DSC, DMTA and deflection under load are suitable for off-line determination of degree of cure in a laboratory environment.

3 Overview of Main Cure Monitoring Techniques

The principal cure monitoring techniques, covered here in detail, are:

- temperature
- acoustic
- ultrasonic
- dielectric
- fibre optic strain sensing.

3.1 Temperature Measurements

Temperature is the simplest and most basic quantity which should be measured during material processing. The technology is well-established and a broad variety of sensors provide for any robustness, access restrictions, range, sensitivity or contact/non-contact requirements. Temperature is commonly measured alongside other cure monitoring data to account for inevitable temperature sensitivity of other sensors and is used routinely to control process equipment.

It is often useful to monitor both the material and environment temperature in order to identify exotherms or other temperature dependent material behaviour which does not directly reflect variations in the ambient temperature.

Both peak temperature and the time taken to reach the peak can be used as guides to the “normality” of cure. The maximum temperature obtained can be used to indicate the maximum reaction rate of the material. The location of the sensor and the component size/geometry should be identical for direct comparisons to be made, ensuring the same heat generation and dissipation in all cases.

Amongst the most commonly used sensors available are:

- infrared/thermal imaging
- resistance temperature detectors (RTDs)
- thermochromic paints/coatings/liquid crystal sheets (TLCs)
- thermocouples.

3.1.1 Thermal Imaging

Infra-red (IR) imaging uses a 2-D array of IR radiation detectors and converts the detected energy levels into an image using a colour scale, shown in Figure 3.1. The energy levels are usually selected relative to the area viewed, so the temperature range in the viewing frame affects the sensitivity. The IR detectors used often require cryogenic cooling to function. The advantages of this technique are that it has large area measurement capability and is non-contact. There is also a single point version of the technique known as IR pyrometry.

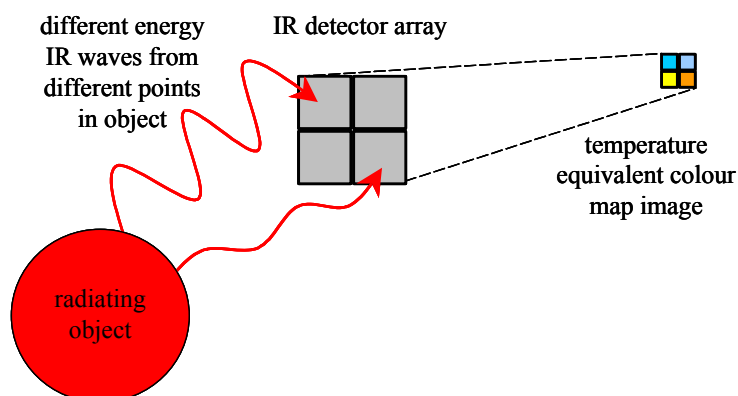


Figure 3.1 - Basic imaging process of infra-red thermography.

3.1.2 Resistance Temperature Detectors

An RTD sensor is either a wire coil or thin film of pure metal. RTDs operate by employing the known temperature dependence of the electrical resistance of the sensor metal. Usually, the hotter the metal, the larger the measured resistance. The resistance is measured by applying a current to the sensor and monitoring the resulting voltage. The most common of these RTDs is the platinum resistance thermometer (PRT). These are nearly linear over a wide range of temperatures, have quick response times and resolutions of 0.1 °C. They also offer good repeatability, stability and low cost, but can be fragile. Errors in calculated temperature due to cables/noise, particularly where long lead lengths are used, can be minimised by connecting the RTD using a 4 wire bridge configuration, shown in Figure 3.2.

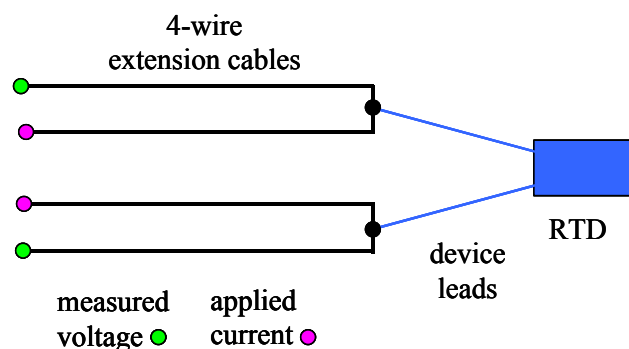


Figure 3.2 - Four wire connection for an RTD device.

The conversion equation for a common PRT, a PT100, from temperature, T , to resistance, R_T , for $T > 0\text{ }^{\circ}\text{C}$ is:

$$R_T = R_0 (1 + 3.9083 \times 10^{-3} T - 5.775 \times 10^{-7} T^2)$$

This gives a conversion constant of roughly $0.385\text{ }\Omega/^{\circ}\text{C}$, where R_0 is the measured resistance at $0\text{ }^{\circ}\text{C}$ (nominally $100\text{ }\Omega$ for a PT100).

3.1.3 Thermochromic Devices

Thermochromic labels/stickers, or paints change colour above a certain temperature. These are single use devices. These are simple, useful and inexpensive allowing a quick assessment of operation within normal temperature boundaries.

Thermochromic liquid crystal sheets function similarly but change colour continuously over a variety of limited temperature ranges, providing a visual colour check of temperature and its distribution over a surface, an example of which is shown in Figure 3.3. These devices are re-usable.



Figure 3.3 - Example of TLC operation: a hand in contact with the sheet shows a colour change compared to ambient.

3.1.4 Thermocouples

Thermocouples are the most widely used and readily available temperature sensor. They consist of two dissimilar metal wires connected together at a welded junction. These work due to an effect experienced by conductors with temperature gradients along their length. They generate a thermoelectric voltage between the open ends according to the size of the temperature difference between the sensing junction and the open ends, as shown in Figure 3.4. This voltage is then interpreted as temperature if the reference temperature of the open ends is known. Despite the non-linearity of the output, the conversions are well known and are often built-in to data capture equipment. Different types, (J, K, T, R etc) have different sensitivities and working ranges with different strengths and weaknesses and should be selected according to application requirements. They have fast response times, are cheap and robust and can operate to very high temperatures. Unlike RTDs, these do not require an external power supply to function.

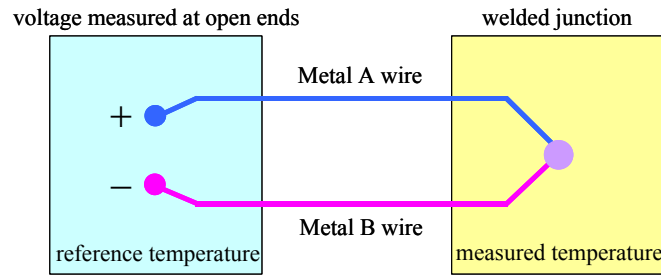


Figure 3.4 - Principal of operation of a thermocouple.

3.2 Acoustic Natural Frequency Measurements

The principle of this non-destructive method is to induce a vibration in a curing component by either a mechanical impulse or by sound wave excitation. A transducer detects this vibration and the signal produced is analysed [4].

The frequency spectrum of this vibration depends on the resonant frequencies which are affected by:

- elastic properties of the curing material
- component geometry
- material density.

The amplitude of the resonant frequency peaks is often also a useful indicator of these material properties.

Changes in density occur during the cure reaction, so the resonance is a relative measure of the combined effects of the material stiffness and density.

3.2.1 Impact Excitation

Impact excitation methods are mostly used to determine the state of cure/dimensional tolerance of a finished part. The method set-up is shown for a simple shape in Figure 3.5.

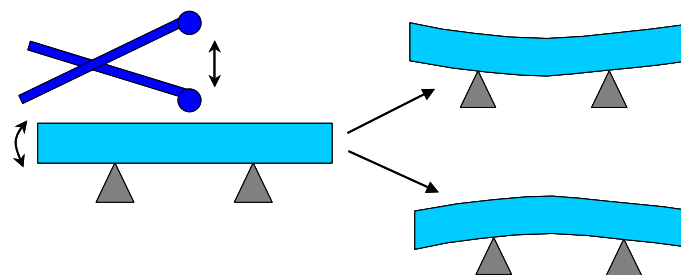


Figure 3.5 - Flexural vibration of a simple rectangular bar.

The part is suspended on thin taut wires. A small striking implement is used to impact the component on a specified point. The point which is struck, as well as the type of support, determines the resonant modes which are excited (torsional, longitudinal, flexural etc or mixtures thereof) and so for direct comparisons, particularly with complex shapes, this should be carefully controlled. Locating supports at the nodal points of the vibration reduces any unnecessary set-up induced damping. For simple shapes vibration modes and nodes are well-defined. Impacts can be performed manually or using electromagnetically controlled devices, but the strike should be instantaneous to avoid dampening any vibrations in the component through prolonged contact with the striker.

A microphone placed close to the part captures the sound generated and this undergoes spectral analysis to determine the frequency content and hence any deviations from set product limits.

Laboratory curing measurements can be conducted if a sample of the curing material is contained within a stiff “ringing” container. The resonant frequencies can then be seen to shift higher as the material stiffens, from gelation through to final cure and is sensitive to small changes in cross-linking levels even in well-cured material. The resonant peak amplitudes are seen to simultaneously increase as the damping properties of the hardening material decline.

3.2.2 Sound Wave Excitation

This method uses broadband low frequency sound wave pulses, produced by a transducer, to generate resonance in the curing product. The sound waves

are transmitted through solid rod waveguides in direct contact with the material, as shown in Figure 3.6. This signal travels across the component to the receiving transducer/waveguide combination, situated some distance away.

The received signal is monitored and the frequency corresponding to the peak amplitude is recorded from the resulting spectrum. As the stiffness of the material increases, so the resonant frequency increases thus reflecting the increased rigidity. This method gives an immediate indication of the increase in material modulus as cure proceeds.

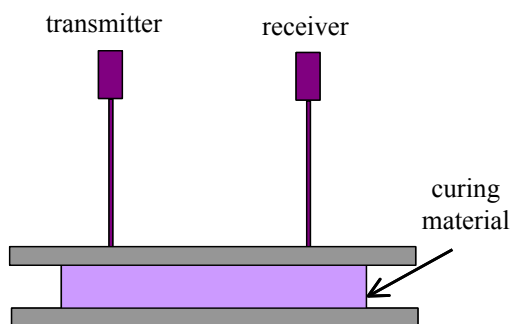


Figure 3.6 - Set-up for acoustic cure monitoring of an adhesive bond.

This method shows fewer problems with attenuation and scattering than the higher frequency ultrasonic techniques. It is robust enough for use in industrial environments and waveguides enable access to closed mould processes. In addition, it provides a measure of a parameter which can be directly related to the performance of the component, i.e. modulus.

3.3 Ultrasonic Velocity Measurements

The speed of sound in a material is dependent on its density and modulus. This fact is exploited in the use of ultrasound velocity measurements in cure monitoring applications [5, 6, 7]. Hence, the time of flight can reflect the state of cure directly where thickness and density variations are negligible.

If the density is also known, then the ultrasonic velocity can subsequently be used to determine the modulus of the material. This can be challenging as density changes with cure progress and temperature, so ultrasonic velocity is reported as a relative measure of the combined materials properties.

For compression waves, the ultrasonic velocity, v , in a material of density ρ is directly related to its modulus, E , using:

$$v \propto \sqrt{(E / \rho)}$$

The ultrasonic velocity increases as cure progresses giving an immediate indication of the increase in product density and mechanical stiffness. Alternative parameters which can be measured include peak frequency and peak amplitude.

Ultrasonic measurements can be made in two ways, using either compression or shear waves:

- through-transmission
- pulse-echo.

Shear waves are more sensitive to the end of cure when most of the network structure has developed but are more difficult to apply in practice, so compression waves are most often used.

3.3.1 Through-Transmission

For the through-transmission technique, two transducers are required, aligned collinearly. An electronic excitation unit produces a voltage spike which triggers a pulse of ultrasound from the transmitting transducer. The pulse travels through the material and is received by the second transducer, as shown in Figure 3.7.

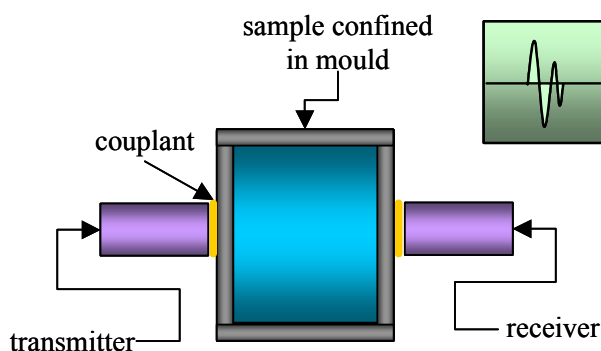


Figure 3.7 - Ultrasonic through-transmission set-up, with (inset) typical received signal.

The received signal, which may be amplified, is then captured and displayed on a PC. A distinctive feature of the pulse, e.g. a baseline crossover, is then used to time the passage of the ultrasound from one probe to another. The timings need to be resolved down to approximately 1 ns to ensure the required sensitivity for cure monitoring.

These measurements are repeated at regular intervals during processing to produce a trace directly related to the material properties throughout cure. This procedure can be automated using software control and analysis.

The availability of robust high temperature ultrasonic transducers and coupling media enables this method to be used for high temperature processes. In this case, the system needs to be calibrated for variations in the transducer response with temperature.

The inclusion of transducers into tool walls, within a few mm of the material, enables this method to be employed in enclosed processing environments.

The frequency, power and transducer diameter determine the maximum thickness/attenuation of material which can be investigated.

3.3.2 Pulse-Echo

Pulse-echo is based on the same principles of ultrasonic time of flight, but here only a single transducer is used, as shown in Figure 3.8. A pulse is sent through the material and, at the boundary between the material and air or mould wall, the pulse is partially reflected due to the acoustic impedance mismatch. This reflected signal is then captured by the same transducer and the transit time determined.

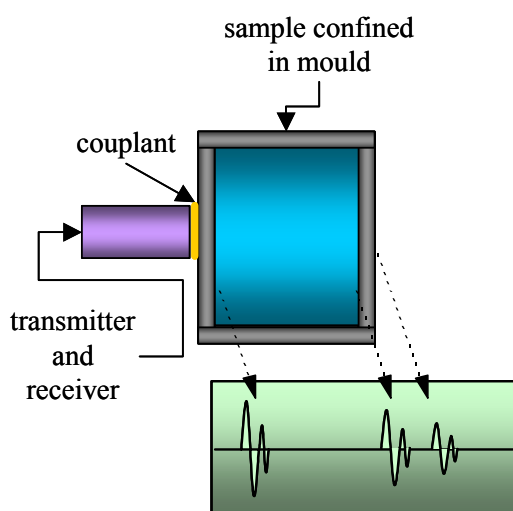


Figure 3.8 - Ultrasonic pulse-echo set-up, with (inset) typical received signal showing additional reflected signals from mould walls.

Pulse-echo has limited use for very thick or high attenuation material, since the pulse travels through the sample twice and experiences twice the signal loss. It is also limited by the complex reflected signal received from multiple interfaces (especially filled polymers such as fibre-reinforced composites) and interference between transmitted and received signals. Some restrictions would exist for thin coatings where the sample signal would be masked by the ringing triggered by the excitation pulse.

However, this method is ideal where only one-sided access is available, it is also more sensitive than through-transmission (twice the transit time therefore twice the difference in the measured time of flight) and has correspondingly lower equipment costs.

3.4 Dielectric Measurements

This technique uses electrodes in contact with the resin to monitor the evolution of the intrinsic electrical properties of the material, occurring due to chemical and physical changes during cure (viscosity and T_g).

The basic principle of operation is the measurement of changes in the voltage and current between a pair of electrodes. This method is purportedly the most comprehensive at detecting all of the important stages during cure, despite the seemingly abstract nature of dielectric properties and uncertainty in their relevance to processing parameters.

The application of a sinusoidal voltage to a pair of electrodes creates a localised electric field. This induces ion motion and dipole rotation within the resin generating a sinusoidal current. These motions are hindered by viscous drag, resulting in a phase difference between the applied voltage and the stimulated current, as shown in Figure 3.9.

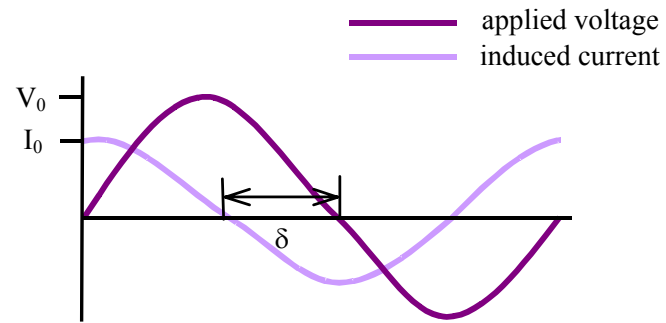


Figure 3.9 - Amplitude and phase relationship between applied voltage and current response.

This charge redistribution and reorientation only occurs whilst the charged species are sufficiently mobile to respond within the timescale/frequency of the exciting field. By measuring the current and associated voltage at regular intervals and several frequencies as cure progresses (as wide a range as possible within 10^{-4} - 10^{11} Hz), the changing conductance and capacitance of the resin can be determined.

The electrical properties may be expressed in different ways, from the measured voltage, V_0 , and current, I_0 , and phase shift, δ .

The most basic method is the complex impedance, Z . This defines the a.c. electrical resistance, and thus comprises phase angle information. Z is determined by (' - indicates the "real" part or the in-phase response and " - indicates the "imaginary" part or the 90° phase-shifted response):

$$Z = Z' - i Z''$$

$$|Z| = \sqrt{(Z'^2 + Z''^2)} = V_0 / I_0 \quad \text{and} \quad Z'' / Z' = \tan \delta$$

This can be converted to dielectric permittivity, ϵ , which defines the ability of the material to store charge from the applied field [8], using:

$$\epsilon = \epsilon' - i \epsilon''$$

$$\epsilon' = -Z'' / \omega C_0 Z^2 \quad \text{and} \quad \epsilon'' = -Z' / \omega C_0 Z^2$$

where $C_0 = \epsilon_0 A / d$ is the vacuum geometric inter-electrode capacitance of the cell; ϵ_0 is permittivity of vacuum (8.854×10^{-12} F/m) and A / d is the cell constant which is dependent on the electrode spacing.

3.4.1 Theory

The analysis used in the interpretation of dielectric data depends on the particular behaviour of the material under investigation, which may change between early and later stages of cure, hence:

- dipolar component - dominates at high frequency and high viscosity, such as after gelation, and
- ionic component - dominates at low frequency and low viscosity, such as prior to gelation, as well as at high temperatures.

3.4.2 Equivalent circuits

It is convenient to use electrical circuits made up of resistors and capacitors to represent the electrical characteristics of a resin, analogous to the spring and dashpot models used to describe viscoelasticity.

Different equivalent circuits can be used to describe materials exhibiting particular behaviour [9]:

- relaxation - series circuit (these materials show a peak in ε'' or dielectric loss factor),
- conduction - parallel circuit (these materials show a peak in Z'' or imaginary impedance), and
- relaxation and conduction - combined circuit.

Examples of the expected electrical response for each of these types of material behaviour are presented in Figure 3.10.

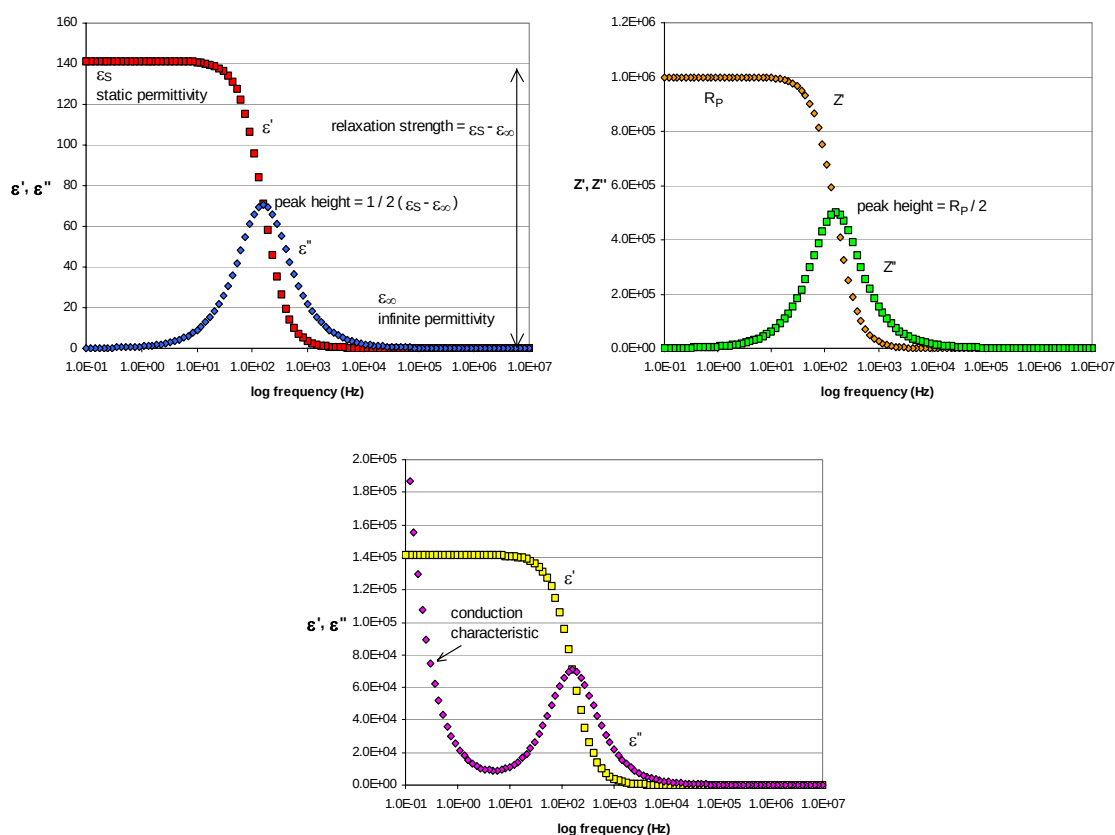


Figure 3.10 - Typical material responses to an electric field: relaxation (top left), conduction (top right) and combined conduction and relaxation (lower).

For a resistor, R_S , and capacitor, C_S , in series:

$$Z = R_S + 1 / i \omega C_S$$

where ω is the angular frequency of the applied field. For a resistor, R_P , and capacitor, C_P , in parallel:

$$Z = (R_P - i \omega C_P R_P^2) / (1 + \omega^2 C_P^2 R_P^2)$$

These model systems are complicated by additional factors, other than charge migration and dipole orientation, when studying real materials [10]:

- electrode polarisation - accumulation of ions at the polymer-electrode interface, and
- interfacial or space charge polarisation - accumulation of charges at boundaries in heterogeneous systems.

Electronic polarisation (displacement of electrons in an atom from equilibrium) and atomic polarisation (deflection of atoms in a molecule from equilibrium) in the presence of an electric field are considered instantaneous effects, forming the minimum background polarisation levels due to an applied field in the frequency range μHz to GHz .

3.4.3 Dielectric permittivity (ϵ)

For a material showing relaxation, the dielectric permittivity can be described with the following expression as:

$$\epsilon(\omega) = \epsilon_\infty + (\epsilon_S - \epsilon_\infty) / (1 + i \omega \tau)$$

where $\epsilon_S - \epsilon_\infty = C_S / C_0$ and $\tau = R_S C_S$.

Here, as demonstrated in Figure 3.10, ϵ_∞ (at high frequencies) represents the contribution of atomic and electronic polarisation to the dielectric constant, ϵ' , and ϵ_S (at low frequencies) represents the highest degree of dipole orientation attained for a particular temperature and field. The relaxation time constant, τ , defines the polarisation decay time upon removal of the exciting field and is a fundamental material property.

3.4.3.1 Relaxation strength ($\Delta\epsilon'$)

Another approach is based on the characterisation of the extremes in dielectric constant, ϵ_∞ and ϵ_s , or the difference between them, $\Delta\epsilon'$, which changes systematically during cure at a particular temperature.

ϵ_s is directly related to the material's dipole composition. It increases linearly with degree of cure and decreases with increasing temperature, whereas ϵ_∞ is independent of these factors.

The primary requirement is a polar nature of either a reactant or one of the products of the cure reaction. In the early stages of cure the decrease in ϵ' is gradual, with an abrupt drop when the system vitrifies, as shown in Figure 3.11. ϵ' should be monitored at a frequency where electrode polarisation is negligible.

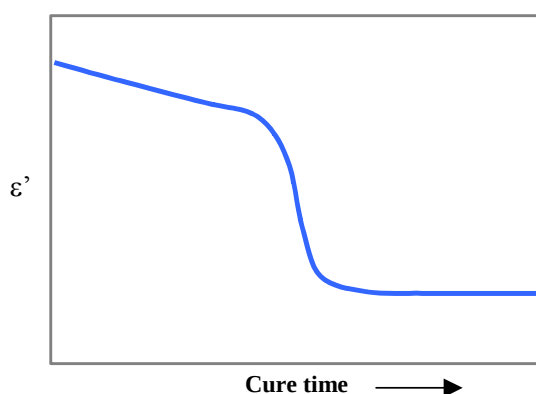


Figure 3.11 - Evolution of ϵ' with degree of cure.

3.4.3.2 Dipole polarisation relaxation time (τ)

The average relaxation time of the curing system increases as the glass transition temperature increases ($\log \tau$ is proportional to T_g^2). Consequently the loss peak in ϵ'' , which occurs at a frequency $f_{\max} = 1 / 2\pi\tau$, shifts to lower frequencies with degree of cure under isothermal conditions. Vitrification is assumed when the relaxation time reaches 1 Hz. This method can also be used to predict vitrification times by extrapolation, as shown in Figure 3.12, although subtraction of the ionic contribution may be necessary for this to be successful.

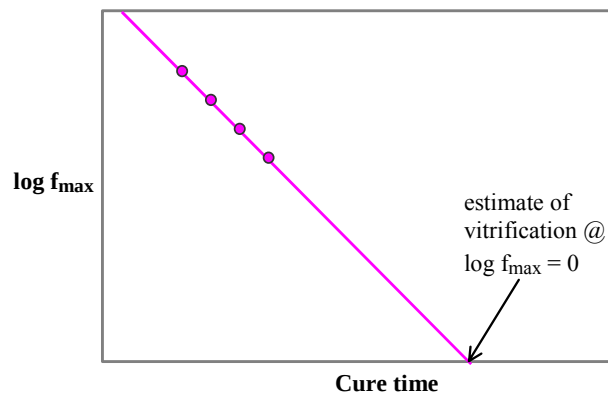


Figure 3.12 - Change in relaxation time with degree of cure.

3.4.3.3 Conductivity (σ)

Charge migration affects the dielectric loss, ϵ'' , adding an extra dissipative contribution [11] such that:

$$\epsilon'' = (\epsilon_s - \epsilon_\infty) \omega \tau / (1 + \omega^2 \tau^2) + \sigma / \omega \epsilon_0$$

At frequencies where conduction dominates:

$$\epsilon'' \approx \sigma / \omega \epsilon_0$$

Conductivity, σ , is a convenient measure of cure up to the gel point. Prior to the gel point, resin viscosity is inversely proportional to conductivity. Several notable cure stages can be deduced from the conductivity [12], shown schematically in Figure 3.13:

- minimum resin viscosity - corresponds to the maximum in the plot of ionic conductivity with cure time,
- gel point - qualitatively found from point of inflexion on the log conductivity with cure time plot (or the zero slope on the time derivative of the log conductivity, DLIC, or the zero point on the second derivative of conductivity with time, D^2LIC), and
- reaction completion - time derivative of conductivity plotted with cure time is qualitatively similar to the rate of cure such that the plateau region indicates the maximum degree of crosslinking.

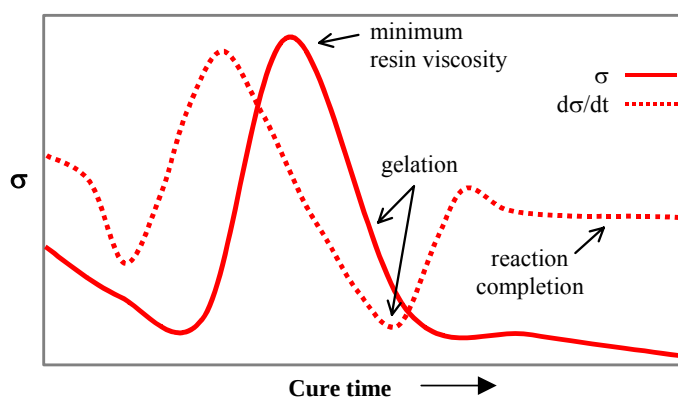


Figure 3.13 - Typical conductivity–time profile.

Conductivity should be the same for all frequencies if not significantly affected by dipole relaxation (at high frequencies) or electrode polarisation (at low frequencies < 50 Hz). If an apparent frequency dependence is observed then the frequency range of conductivity measurement should be changed to a more insensitive region.

3.4.4 Impedance (Z)

The impedance spectrum can be used in a similar way to the dielectric response of a curing system [13]. For a material showing conduction, the impedance is described as:

$$Z(\omega) = R_p / (1 + i \omega \tau)$$

where $\tau = R_p C_p$.

The real impedance Z' exhibits dispersion-type behaviour dropping from a maximum plateau value of R_p at low frequency to zero at high frequency, shown in Figure 3.10.

A plot of the imaginary impedance spectrum, Z'' , shows a minimum and a maximum. As cure progresses under isothermal conditions, the values of these minima and maxima increase but shift to lower frequency positions, as shown in Figure 3.14.

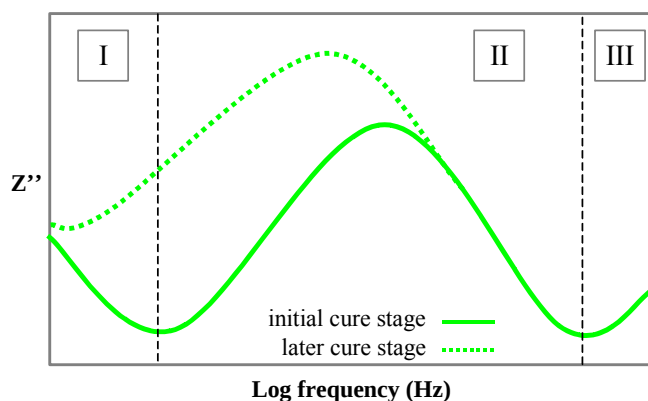


Figure 3.14 - Typical imaginary impedance profiles at different stages of cure.

This schematic also highlights that the conduction dominated zone at intermediate frequencies (zone II) can be clearly identified from the neighbouring regions dominated by electrode polarisation at low frequencies (zone I) or dipolar relaxation at high frequencies (zone III).

Impedance profiles enable the conductivity to be calculated from the imaginary impedance peak without interference from phenomena which dominate in the adjacent zones, using:

$$Z''_{\max} = R_p / 2 \quad \text{and} \quad \sigma = 1 / 2 Z''$$

A plot of $\log Z''$, normalised with respect to the difference between the minimum and maximum values, with time qualitatively resembles a sigmoidal extent of cure trace.

3.4.4.1 Frequency shift ($f_{\max} - f_{\min}$)

The combined effects of temperature and material state during dynamic cure can complicate the simple changes in the imaginary impedance profile described in Figure 3.14. The maximum and minimum both shift to higher frequencies with increasing temperature and to lower frequencies with increasing degree of cure.

The temperature shift for both the maximum and minimum values are similar, but a disparity occurs with the cure-induced shift such that the minimum displays a greater cure sensitivity [14].

This fact can be used to eliminate the effect of temperature from these observations giving plots of $\log (f_{\max} - f_{\min})$ with cure time which resemble fractional cure conversion curves. A typical example of this is shown in Figure 3.15.

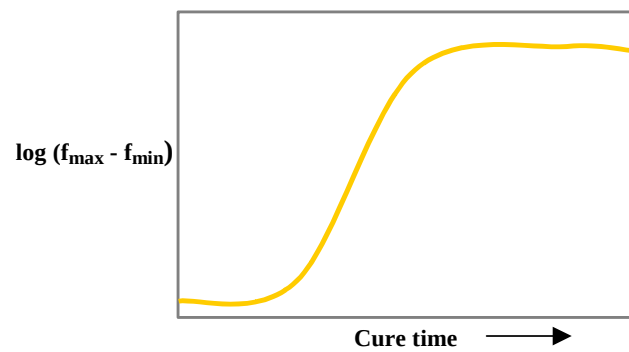


Figure 3.15 - Change in impedance maxima and minima frequencies with cure.

3.4.5 Dielectric sensors

There are several electrode configurations available, as shown in Figure 3.16. The two principal types are:

- inter-digitated sensors, and
- parallel plate or bulk sensors.

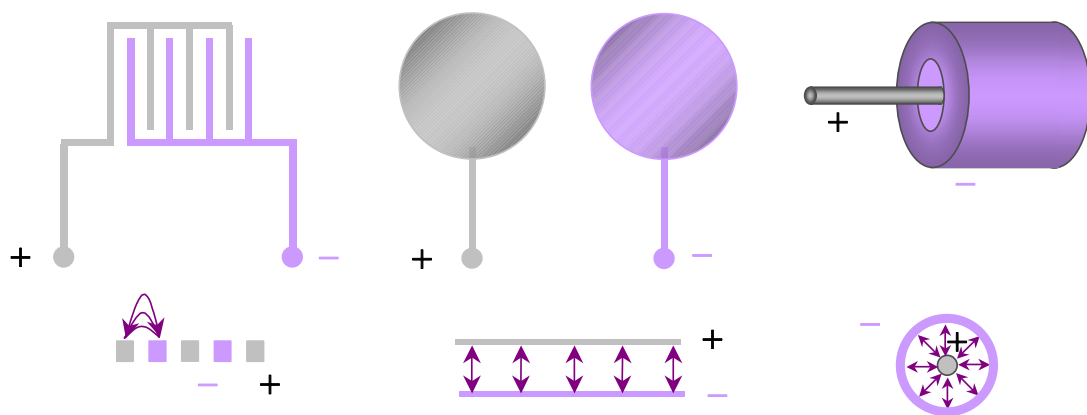


Figure 3.16 - Basic dielectric sensor configurations and their resultant electric fields: inter-digitated (left), parallel plate (centre) and coaxial (right).

Inter-digitated sensors are single surface, comb-like metallic electrode patterns printed onto a small, thin insulating substrate layer. They produce localised fringing fields, between adjacent electrode fingers of opposite

polarity, extending out into the resin to a distance determined by the electrode geometry/spacing.

Parallel plate sensor pairs are solid areas of metallic electrode deposited onto an insulating base. These produce a uniform electric field between the plates of opposite polarity.

Dielectric sensors can be either implanted or reusable, and positioned externally for surface or embedded for internal measurements. In addition, they need protection from shorting against any conductive components within the material, e.g. metallic particulate fillers or carbon fibre reinforcement, but must still remain in intimate contact with the resin during processing. Durable sensors are available which can be mounted as an integrated part of a mould tool wall.

The sensors are connected to an impedance analyser which is used to perform the electrical measurements over a wide frequency range and subsequently collect data at regular intervals during the cure cycle.

3.5 Fibre Optic Strain Measurements

Material strain measurement using optical fibre Bragg gratings is the most developed of the optical cure monitoring methods. This is primarily due to the surge in interest and adoption of structural health monitoring, where gratings are applied to structures usually for in-service applications. The evolution of strain as a means of determining cure progress has not been widely investigated, even though there is increased research into processing-induced residual strains.

This technique uses optical fibres embedded in the resin to monitor the accumulation of strain within the material, due to constrained thermal deformation and chemical shrinkage during cure.

Optical fibres are waveguides used to confine light. They usually consist of silica glass cores surrounded by cladding of a lower refractive index. As a result, total internal reflection occurs at the boundary and light propagates along the fibre core. The typical structure is shown in Figure 3.17. Additional polymer layers provide damage protection.

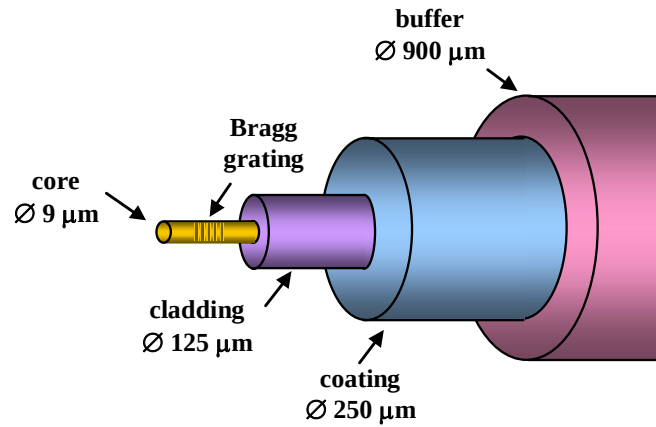


Figure 3.17 - Basic structure of optical fibre with Bragg grating.

A Bragg sensor is a segment of optical fibre with a longitudinal periodic modulation in the core refractive index which acts as a narrowband reflection filter [15]. These segments are typically 3 - 15 mm long.

The basic principle of operation is the measurement of changes in the wavelength of the reflected signal, i.e. centre or Bragg wavelength, when illuminated with a broadband light source. This is shown schematically in Figure 3.18.

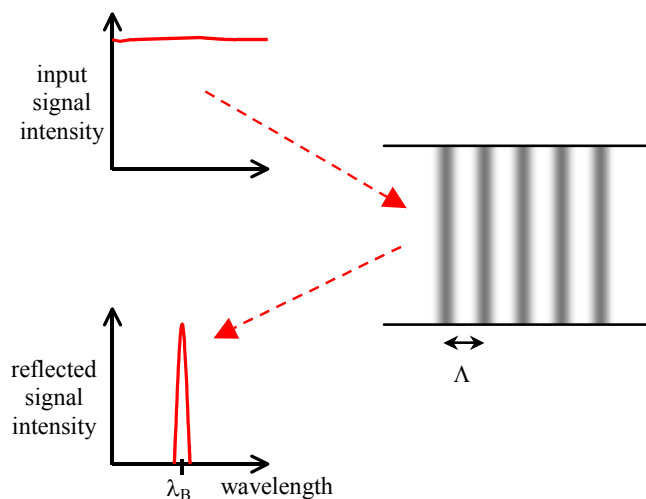


Figure 3.18 - Typical spectral response of a fibre Bragg grating.

The Bragg wavelength is dependent on the effective refractive index of the core, n_{eff} , and the grating periodic spacing, Λ .

3.5.1 Theory

The Bragg wavelength, λ_B , can be expressed as [16]:

$$\lambda_B = 2 n_{\text{eff}} \Lambda$$

consequently any external factors, i.e. mechanical strain, $\Delta\epsilon$, or temperature, ΔT , which act to alter the characteristic grating properties can cause a shift in the reflected wavelength.

For a 'free' fibre this wavelength shift can be expressed:

$$\Delta\lambda_B = \lambda_B (K \Delta\epsilon + \beta \Delta T)$$

where K is the wavelength-strain sensitive factor (typically 1 pm/microstrain) and β is the wavelength-temperature sensitive factor (typically 10 pm/°C). Hence the influence of temperature is 10 times more significant than the effect of strain and so temperature compensation is critical for accurate strain determination. These factors can be reduced further to:

$$K = 1 - p_e$$

$$\beta = \alpha_\Lambda + \zeta$$

where p_e is an effective strain-optic constant and $1-p_e$ is termed the gauge factor of the grating; α_Λ is the thermal expansion coefficient of the fibre/grating and ζ is the thermo-optic coefficient. In simplified terms, these factors make corrections to account for the following:

- strain-optic constant, p_e , - effect of mechanical strain on refractive index,
- thermal expansion coefficient, α_Λ , - effect of thermally induced strain on the grating period, and
- thermo-optic coefficient, ζ , - effects of both the thermal strain and the temperature on the refractive index.

Thus the measurement of changes in the Bragg wavelength incorporates the linear effects of the imposed strain, due to both mechanical and thermal expansion, and the effects of the non-linear properties of refractive index.

A 'constrained' fibre, i.e. one which is embedded within a material, behaves as a 'free' fibre but with an additional contribution from the thermal expansion of the surrounding material. Hence, for a 'constrained' fibre:

$$\Delta\lambda_B = \lambda_B [K \Delta\epsilon + \beta \Delta T + K (\alpha_s - \alpha_\Lambda) \Delta T]$$

where α_s is the coefficient of thermal expansion of the substrate or host material.

4 Laboratory Demonstrations

4.1 Temperature

The value of measuring temperature as a matter of course can be clearly seen in Figure 4.1. The desired cure cycle is shown and compared to the actual oven temperature as measured with a k-type thermocouple, where these are markedly different, either equipment problems need to be rectified and/or corrections to the cure schedule need to be made. Similarly, the sample temperature as measured with a thin film PRT is compared to the oven temperature profile. In this case, a large temperature lag is evident and the recommended schedule produces an exothermic spike $>25\text{ }^{\circ}\text{C}$ over the required maximum temperature dwell. This is sufficient to produce charring within the material. Knowledge of this effect for this material at temperatures $>150\text{ }^{\circ}\text{C}$ enables modifications, such as a lower temperature dwell for a longer time, which would avoid the detrimental effects of overheating.

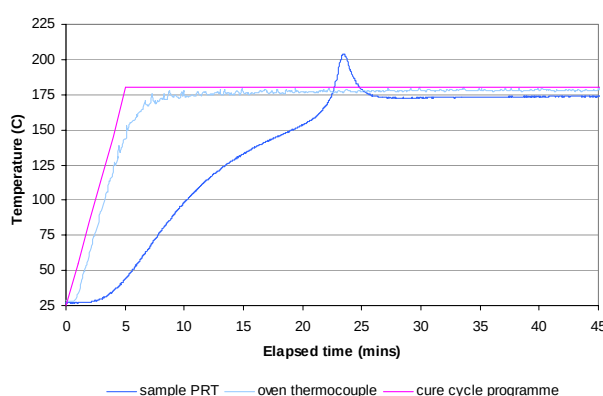


Figure 4.1 - Temperature profiles of surroundings and XD4601 adhesive sample in an oven.

A series of temperature tests were run using both an infra-red imaging camera (calibrated using two set points to enable absolute temperature measurement) and a T-type thermocouple with data logger, on a series of mix ratios for a simple two-part room temperature curing epoxy adhesive. The experimental set-ups are shown in Figures 4.2 and 4.3.



Figure 4.2 - Temperature measurement using T-type thermocouple and cold junction compensating data logger.



Figure 4.3 - Temperature measurement using 2-D infra-red camera.

Initially, the ability of these two techniques to distinguish between the following was investigated:

- correct 1:1 mix epoxy/hardener ratio,
- incorrect 2:1 mix epoxy/hardener ratio, and
- contaminated (20% water) correct epoxy/hardener mix ratio.

The results from these tests are shown in Figure 4.4. They show good correlation between the temperature as determined by the IR camera and that recorded separately from the thermocouple.

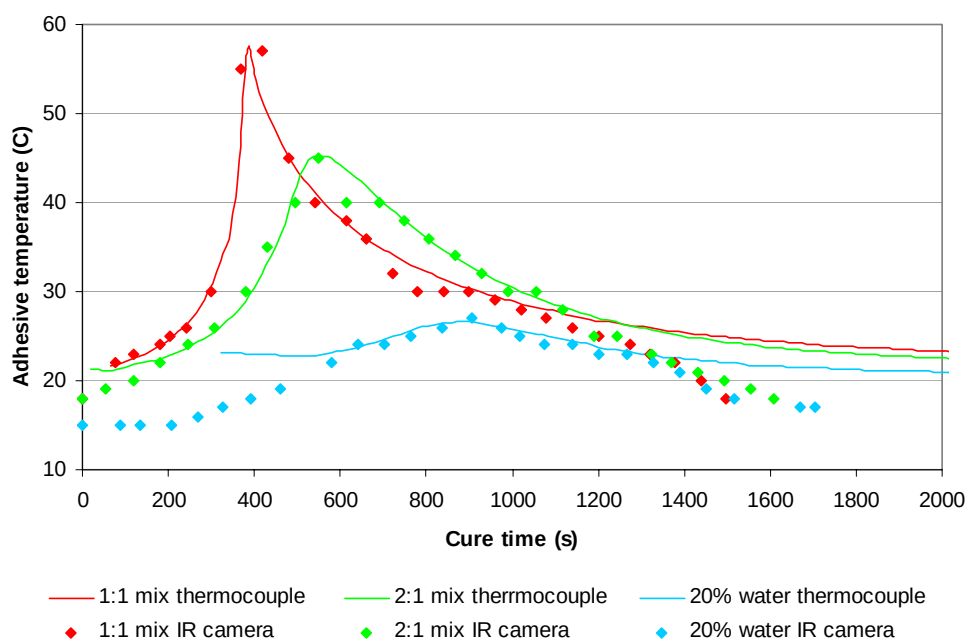


Figure 4.4 - Temperature profiles of room temperature curing epoxy adhesive using T-type thermocouple and IR camera for different mix ratios.

The different mix ratios/contaminations are readily discernable, with the correct mix giving the highest temperature peak and the fastest reaction rate (peak is achieved quicker). This would enable aged material, incorrect or contaminated mixes or other batch problems to be identified by comparison with the temperature profile range as determined for “good” material.

Images captured using the IR camera from the 1:1 mix and the water contaminated mix at their respective peak temperatures are shown in Figure 4.5. These give very distinctive 2-D temperature images for the two mixes, indicating clearly the reduced cure reaction in the contaminated batch and allowing non-standard mixes to be identified simply.

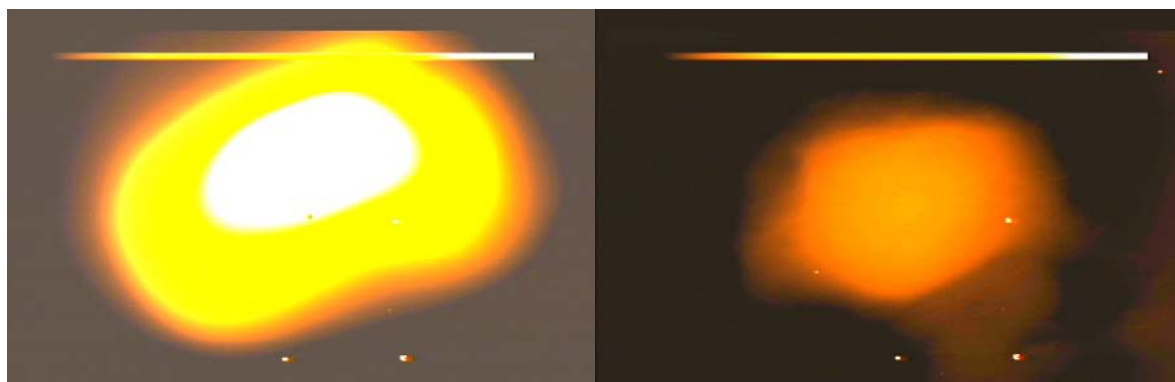


Figure 4.5 - IR camera images of 1:1 mix (left) after 7 mins and 20% water contaminated mix (right) after 15 mins; showing relative peak temperatures.

This effect was further investigated with an extended range of non-stoichiometric mixes. The results from these are shown corrected for room temperature in Figure 4.6, giving relative temperature increases.

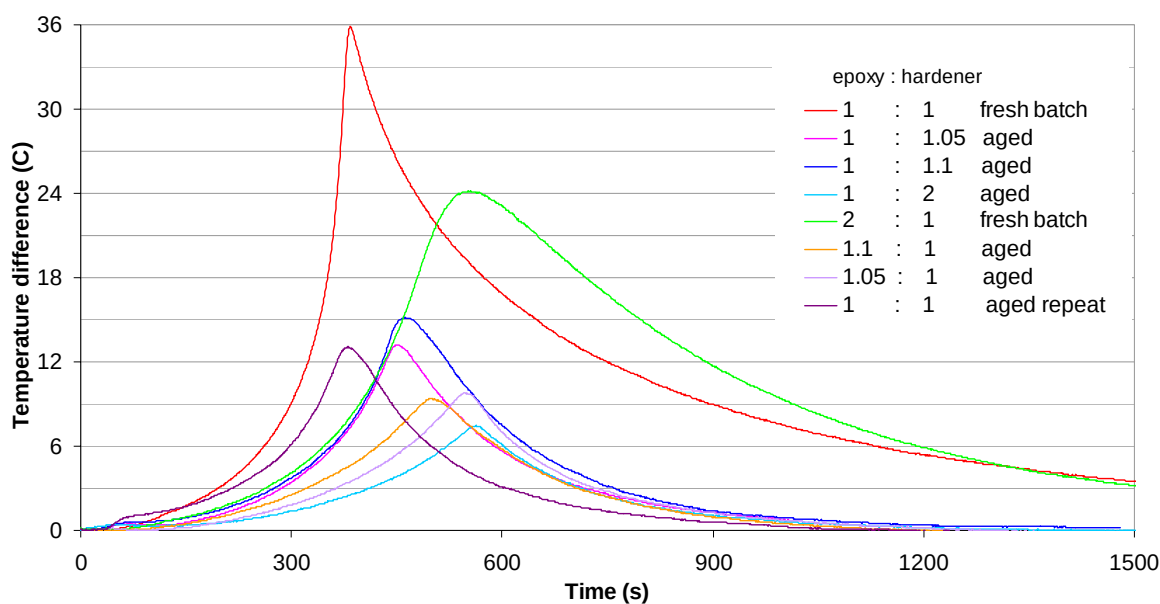


Figure 4.6 - Normalised temperature profiles of 2 part room temperature curing epoxy adhesive using T-type thermocouple for different mix ratios and material ages.

There seems to be an ageing effect between nominally identical 1:1 mixes which is highlighted by the temperature profile. Whilst the peak position of the aged 1:1 mix with respect to time hasn't changed, the peak value has reduced to 55% of the original fresh batch. If we assume something similar

happens to the fresh 2:1 mix, the resulting profile would be similar to the 1:2 mix in terms of time and peak characteristics.

As sample volumes and geometries (surface areas) were not controlled for each test any indications of overall trends are difficult to establish, however, there is a definite retarding effect on the time taken to reach peak temperature (and so on the reaction rate) for non-stoichiometric mixes. The effect of small relative increases in hardener are less significant than small increases in epoxy, but both are less significant than large deviations from the recommended ratio (e.g. 2:1 or 1:2).

Small excesses of hardener have a minimal effect on the peak temperature (allowing for scatter), with small excesses of epoxy having a slightly greater effect. Large changes in the mix ratio (2:1 and 1:2) leave significantly less reactive pairs per unit volume so much less heat is generated regardless of whether the epoxy or hardener are in excess, so reducing the peak temperature reached.

Notes:

- Materials must exhibit a measurable exothermic or endothermic cure reaction for temperature cure monitoring to be applicable.
- The temperature measured will depend on the temperature of the surrounding environment. In this case, it is often more useful to look at temperature change rather than absolute temperature.
- The conductivity and thermal mass of the curing material itself and any substrates/containers it is in contact with will affect the heat dissipation and therefore the maximum temperature achieved within the material.
- The position of the sensor within a component will affect the measured temperature, with highest temperatures at the centre and lowest at the periphery of the material volume.
- The mass, volume, geometry and surface area of the curing material will affect the measured temperature and temperature rise. For comparison purposes, these quantities should be identical.

4.2 Acoustic Natural Frequency

The impact excitation method was investigated using a Resonant Frequency and Damping Analyser (IMCE n.v.). This introduced vibrations into samples by a mechanical impulse (controlled tap) and monitored the signal produced.

Several room temperature curing liquid resins were studied using this method, including:

- 3M Scotch-Weld DP 460 epoxy,
- 3M structural adhesive 5027 epoxy,
- Crystic 196 polyester.

Curing bulk resin samples were placed within glass petri dishes, effectively simulating mould walls. These assemblies were supported on taut wires to allow free vibrations. An automated system was used to trigger an impact on the dish which induced both flexural and torsional modes of vibration, detected using a microphone positioned nearby. The resonant frequencies of the assembly were determined from this captured signal using Fast Fourier Transforms (FFT) giving reproducible frequency “fingerprints”. The assembly was sampled at regular intervals during the cure process to monitor the evolution of these “fingerprints”. A typical set-up is shown in Figure 4.7.

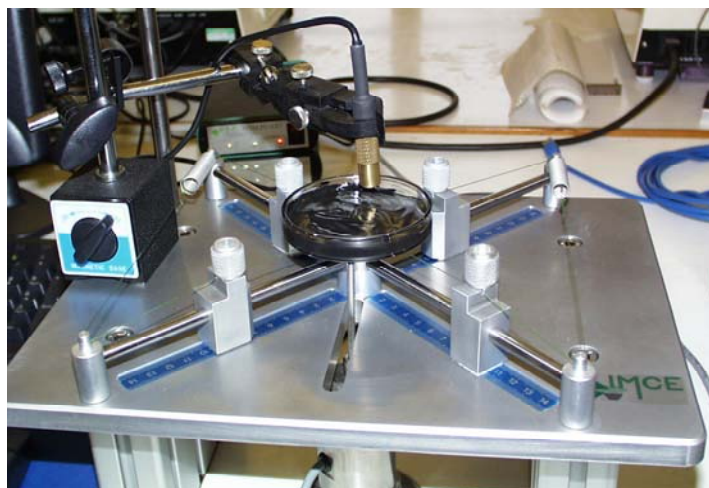


Figure 4.7 - Natural frequency instrumentation.

A typical vibration signal is shown in Figure 4.8. Subsequent FFT analysis produced frequency spectra similar to those shown in Figure 4.9. This shows dramatic differences in both the position of resonant frequencies and in their amplitude after the resin has cured.

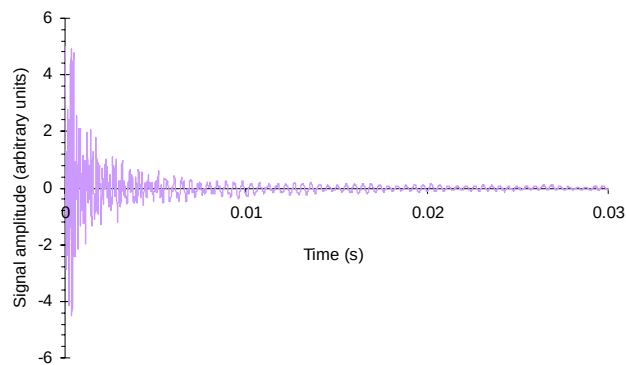


Figure 4.8 - Vibration signal after impact excitation.

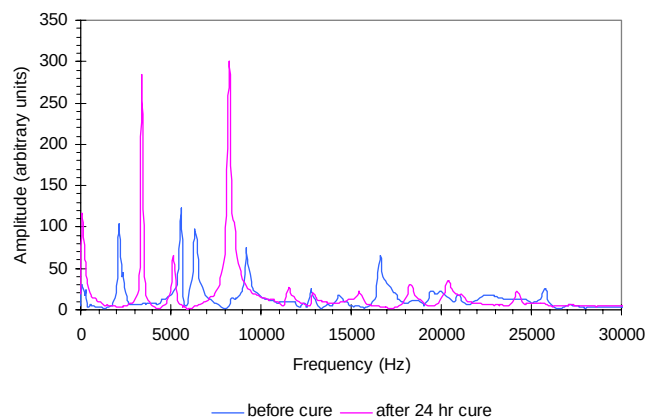


Figure 4.9 - Typical frequency “fingerprints”, in this case from DP460 before and after cure.

The changes in the frequency “fingerprint” as the material viscosity and stiffness changes throughout cure can be seen in Figures 4.10 and 4.11.

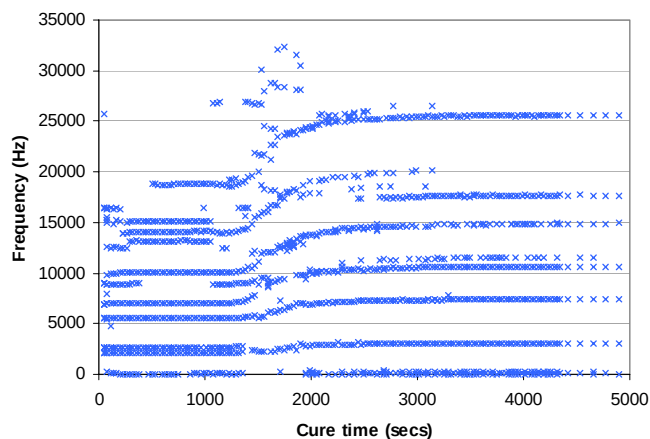


Figure 4.10 - Natural frequency components during cure of Crystic polyester.

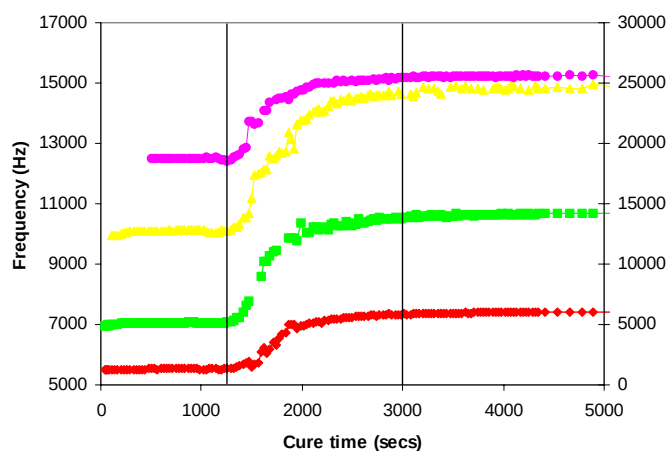


Figure 4.11 - Observed gradual increase in selected frequency components during the cure of Crystic polyester.

These graphs show an initial frequency plateau region correlating to the period during which the resin was liquid, followed by an increase in frequency as the conversion to solid proceeded. This was again followed by a gently upward sloping plateau region once the conversion to solid was essentially completed and further cure was limited.

The point at which the frequencies began to increase was observed to coincide with the point of gelation. The levelling off after the rapid increase in natural frequency was similarly observed to coincide with hardening of the polymer.

This same effect was seen with the other resin systems; although less clearly for the viscous, rubber-filled 5027, as shown in Figure 4.12.

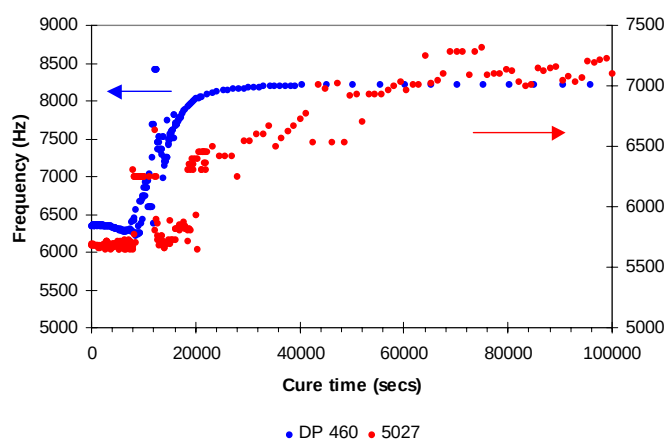


Figure 4.12 - Changes in frequency/cure conversion plots for DP 460 and 5027 resins.

Samples can also be tested in other forms e.g. as coatings or adhesive joints. Consequently, a two part room temperature curing epoxy adhesive was investigated (in flexural vibration mode) as a coating on a thick rectangular aluminium substrate and as a bond layer between two aluminium plates.

The same trend was again seen for the epoxy coated and bonded substrates shown in Figure 4.13, with the frequency changing in line with the degree of cure.

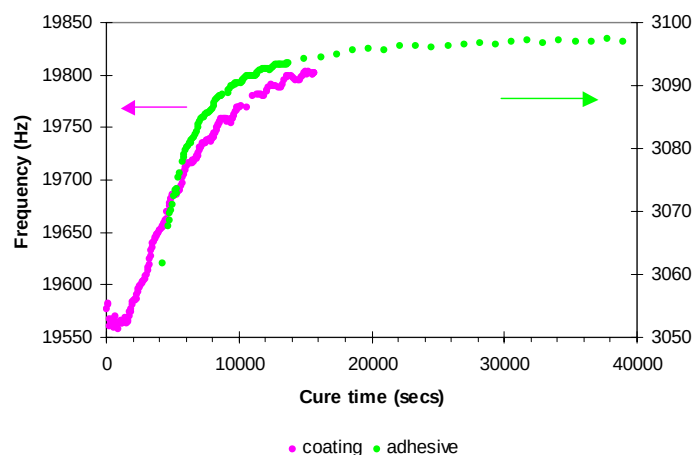


Figure 4.13 - Changes in frequency/cure conversion plots for two part epoxy coated and bonded samples.

Notes:

- For certain specific geometries of cured components, this method can also be used for post-production QA calculation of elastic properties.
- The test can be extended to elevated temperatures by using a waveguide to transmit the vibrations from the material to the receiving transducer.
- Higher frequency components in the “fingerprint” show greater changes due to differences in physical state or viscosity or stiffness and are more effective for cure monitoring.
- As a real-time cure monitoring technique, this works best for materials with a distinctive change in stiffness from uncured to cured state; for rubbery polymers which are very viscous when uncured and remain pliable even when fully cured, the change is less marked.

4.3 Ultrasonic Velocity

These measurements are based on timing the passage of an ultrasonic pulse through a curing material.

A large body of work concerning industrial applications of ultrasonics have shown the method to be successful in determining cure progress and the development of mechanical properties of the curing component. A typical example is shown in Figure 4.14. This clearly demonstrates several stages during cure:

- I - time of flight increases as material temperature rises,
- II - time of flight decreases as material cures turning from liquid to solid with higher ultrasonic velocity,
- III - time of flight increases as material structural network degrades with continued heating (over-cure).

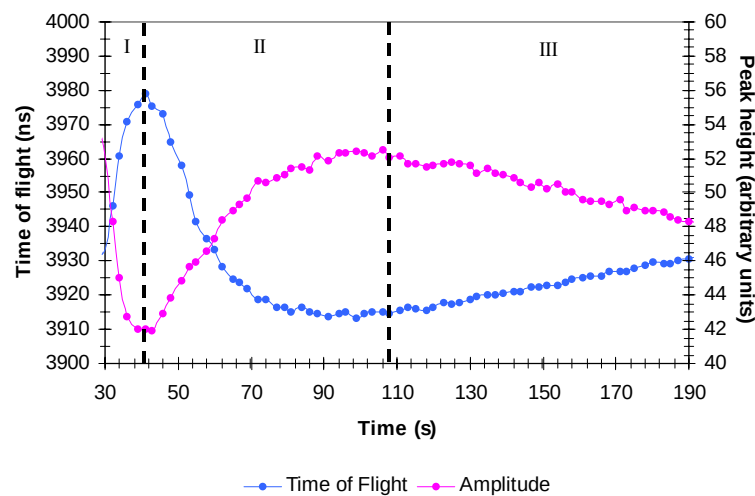


Figure 4.14 - Typical time of flight trace showing changes during elevated temperature cure: I - heating stage, II - curing, III - over-curing.

The most common technique studied is through-transmission where the ultrasound makes a single pass through the material. An alternative arrangement is pulse-echo where the material is monitored from one side and the ultrasound travels through the material twice, being reflected internally.

In this assessment, initial checks were made using a traditional ultrasonic system to check for suitable adaptation to pulse-echo mode operation. A simple trial using a container filled with varying depths of water was conducted, the results from which are shown in Figure 4.15. Figure 4.16 shows an example of an ultrasonic pulse captured using this set-up. This simple test confirmed the capability of the system to detect and analyse pulse echo signals effectively.

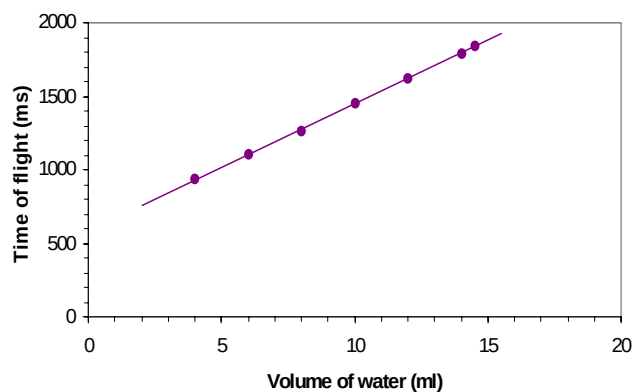


Figure 4.15 - Pulse echo transit times for varying water depths.

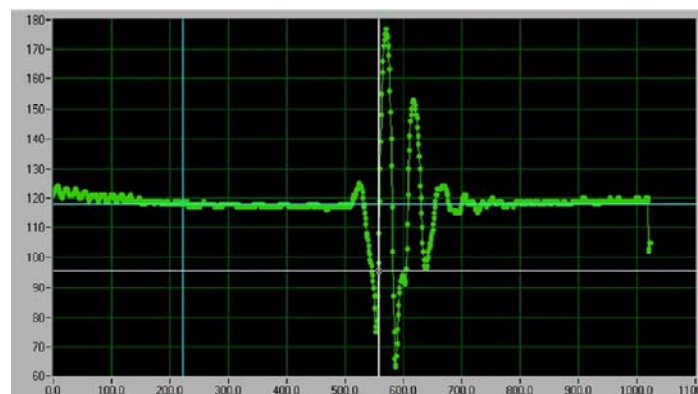


Figure 4.16 - Typical received pulse echo signal.

Subsequently, a sample of DP 460 2-part epoxy was allowed to cure within a container at room temperature, whilst being monitored with a single transducer, as shown in Figure 4.17. The results from this are presented in Figure 4.18 showing the familiar changes in transit time during cure.

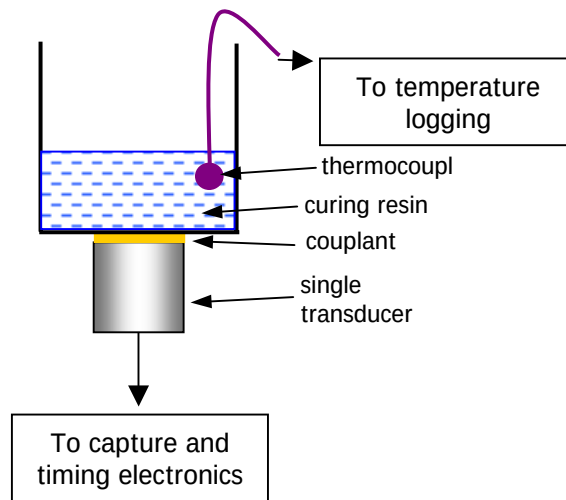


Figure 4.17 - Experimental set-up for pulse-echo measurements on DP 460 epoxy.

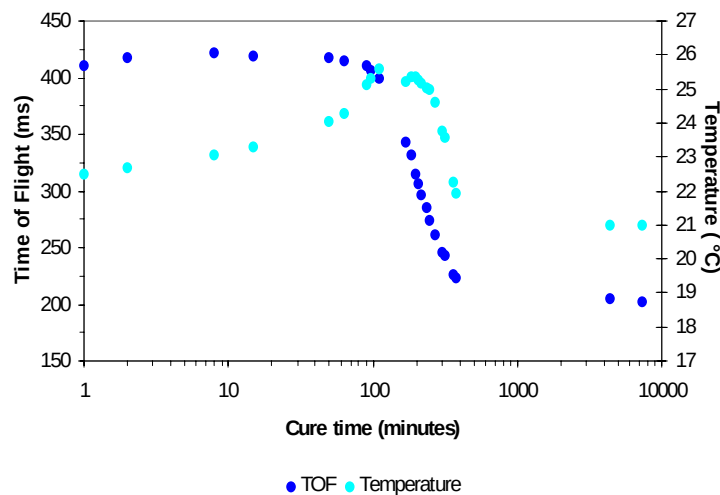


Figure 4.18 - Pulse-echo ultrasonic transit times with degree of conversion for DP 460 resin.

These show the sensitivity of the response of transit time to the level of cure of the material. Small changes seen in the plateau region are caused by the changes in temperature of the material but the large drop in transit time correlates to the onset of gelation. Similarly, the completion of cure is indicated by the onset of the lower plateau, which may still show a small steady drop in transit time as some 3-D links in the material continue to form slowly over a long period of time once the bulk of cure is complete.

Notes:

- Thin materials have a small transit time which would correspondingly show small changes during cure. This may lead to large relative errors and poor sensitivity.
- Signal attenuation through thick materials may be high, such that transmitted pulses cannot be detected at all or are difficult to time accurately.
- Rubbers and highly filled materials, in particular, exhibit high attenuation and large scattering losses respectively, therefore more likely to suffer from low signal-to-noise ratios.
- The crossover timing feature is affected by frequency dependent dispersion, especially in viscoelastic materials.
- It is important to identify relevant signals/echoes where multiple reflections or interfaces are present to avoid confusion and incorrect timing selection.
- Good coupling is required to minimise losses at any interfaces between transducers.
- At high temperatures, specialised robust transducers are required. These must be characterised to compensate for the expected changes in performance at different temperatures.
- The component thickness should be known or at least controlled to a constant value, such that transit time changes can be assigned uniquely to changes in material stiffness/density with cure.
- Changes in temperature will lead to dimensional changes through thermal expansion affecting the time of flight.
- Low frequency, high power and large diameter transducers have better penetration than their counterparts but may exhibit lower sensitivity and resolution.
- Signal capture facilities need to have high time resolution as differences induced by cure can be as low as 1/100 μs .
- Pulse echo signals travel through the target material twice so are more attenuated but show bigger time differences and so are more sensitive to cure changes than through-transmission.
- Pulse echo can suffer from interference between various received signals, depending on their time of arrival.

- Pulse echo on thin samples can be difficult due to ringing triggered by the excitation pulse masking the reflected signal of interest.

4.4 Dielectric

Dielectric measurements were investigated using a broad range of composites and adhesives shown in Table 4.1. In addition, other factors such as the influence of temperature, the measurement hardware configuration and the sensor protective barrier layers were studied.

Table 4.1 - Materials and cure profiles used in dielectric cure monitoring study.

Material	Format	Cure Cycle
SP Systems SPSE90 biax glass/epoxy pre-preg - fresh & shelf aged	composite laminate 8 plies thick	1°C/min 110°C 5 hour dwell
3M Scotch-Weld DP 460 epoxy adhesive - cure & post-cure	adhesive joint Al adherends	25°C > 12 hour dwell
		1°C/min 100°C 4 hour dwell
Dow Chemicals XD 4601 epoxy adhesive - unfilled & metal filled	bulk resin plaque	30°C/min 180°C 2 hour dwell
	bulk resin plaque with 25wt% Cu filings and powder	1°C/min 140°C 8 hour dwell
Hexcel Composites HexPly 924 fabric glass/epoxy pre-preg	composite laminate 10 plies thick	2°C/min 180°C 8 hour dwell
SP Systems SPSE84 ud carbon/epoxy pre-preg - cure & post-cure	composite laminate 14 plies thick	1°C/min 110°C 6 hour dwell
		1°C/min 150°C 4 hour dwell
Hexcel Composites HexPly 913 ud glass/epoxy pre-preg	composite laminate 20 plies thick	2°C/min 125°C 4 hour dwell

The sensors used were 25 x 8 mm area IDEX 066S/067S inter-digitated nickel electrodes with a 115 µm spacing on a polyimide substrate. The sensors (e.g. electrode substrate material or surface barrier layer) and the associated cabling may contribute to the dielectric properties measured from the curing resin. These offsets should not be problematic provided they remain constant throughout the cure cycle, but often they are influenced by temperature such that the sensor response obscures that of the material. This temperature

dependence can be determined experimentally and where necessary deduced from the cure data.

Figure 4.19 shows the temperature response for a number of nominally identical sensors and typical resins. In order to assess the temperature sensitivity of the sensors, a k-type thermocouple was used to monitor bare sensors whilst subjected to ramped heating cycles. The plot shows the responses of individual sensors are relatively flat and broadly similar, but differ by several orders of magnitude from the response of either of the resins. From this, the sensors were assumed to contribute negligibly to the electrical properties of the resin and were not corrected for in subsequent tests.

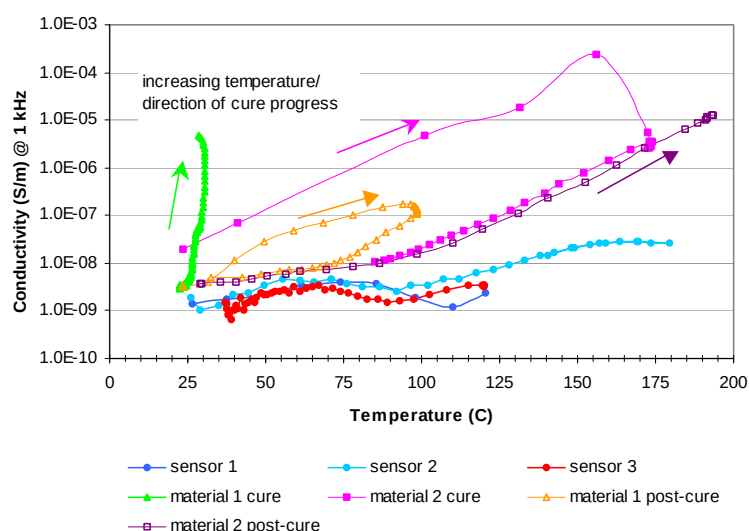


Figure 4.19 - Temperature dependence of dielectric sensor response.

Experiments were also run to ascertain the most appropriate hardware and software configuration by comparing the measured output to that expected for a model circuit (parallel R-C), and from a model material (amorphous polycarbonate at 165 °C).

Figures 4.20 and 4.21 show selected results. The set-up used in these examples gave the closest response to that expected from both the model circuit and material, with the least noise, and so was used for subsequent cure measurements.

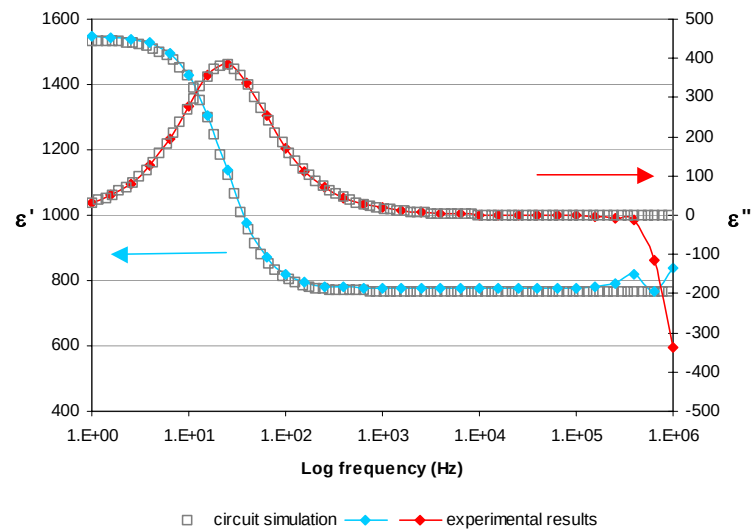


Figure 4.20 - Dielectric profile produced by parallel R-C circuit.

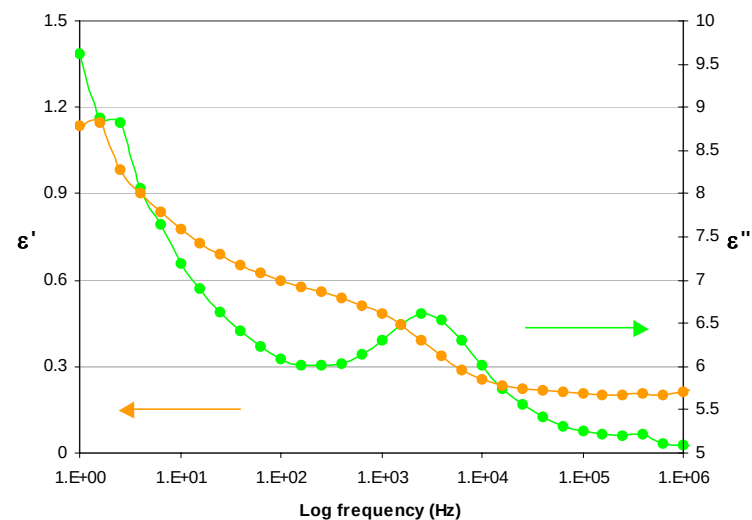


Figure 4.21 - Dielectric profile from polycarbonate at 165 °C.

This configuration comprised:

- Solartron 1296 dielectric interface + 1260 impedance gain-phase analyser using internal reference mode,
- simple unscreened, temperature resistant wires to connect sensor to analyser,
- frequency range 1 - 10⁶ Hz,
- 1 V_{rms} applied exciting field,
- 5 data points/decade (31 points/sweep),
- 3 cycle average per data point, and

- total sweep time ~ 1 min 45 secs.

The set-up performs electrical measurements over a wide frequency range and collects data at regular intervals during cure. Another possibility uses an appropriate single interrogation frequency. This is particularly necessary for fast curing resins where the material can change dramatically over the time otherwise normally taken to do one frequency sweep.

Bare sensors were used in all cases except with conductive materials, where a glass tissue and PTFE coated woven glass screen were used to cover the electrodes. The sensors were positioned in the central region of the material mid-plane. A k-type thermocouple was placed adjacent to the sensor to monitor the local resin temperature. This arrangement can be seen in Figure 4.22 for a conductive pre-preg system.

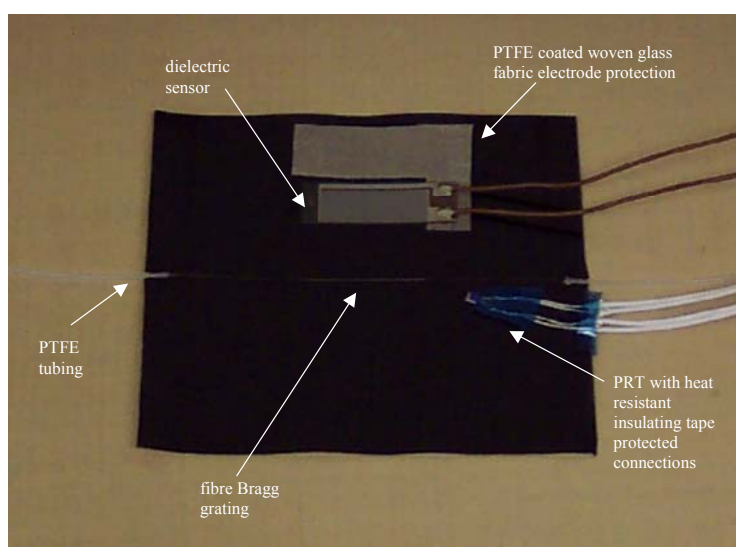


Figure 4.22 - Typical set-up for dielectric and Bragg cure monitoring in conductive SPSE84.

Most of the materials tested displayed conduction behaviour, indicated by Z'' maxima, typical examples of which are presented in Figure 4.23.

These clearly show the characteristic changes expected in plateau level and the peak shift with time that occur during isothermal cure. This response would be modified by the effects of temperature changes under conditions of dynamic thermal cure.

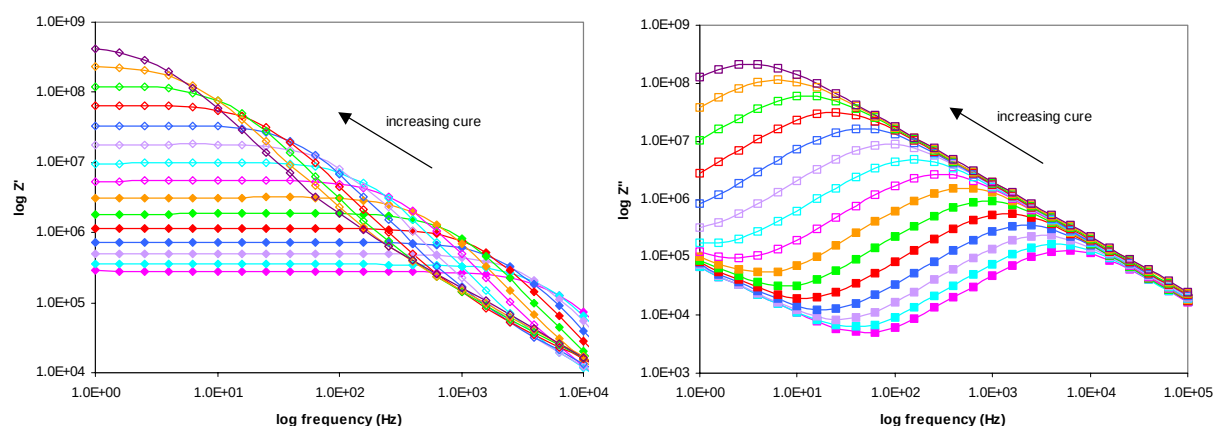


Figure 4.23 - Real and imaginary impedance profiles during room temperature cure of DP 460 epoxy.

Examples of typical analyses are shown graphically in Figures 4.24 – 4.26 using:

- conductivity and its time derivatives,
- maximum imaginary impedance, and
- normalised imaginary impedance.

These indicate the important features used to identify different cure events and the interchangeable nature of the Z'' maximum and conductivity as determined at 1 kHz. However, the Z'' minimum/maximum frequency shift analysis proved unsuccessful in all cases and may only be applicable in a very limited number of instances for specific materials.

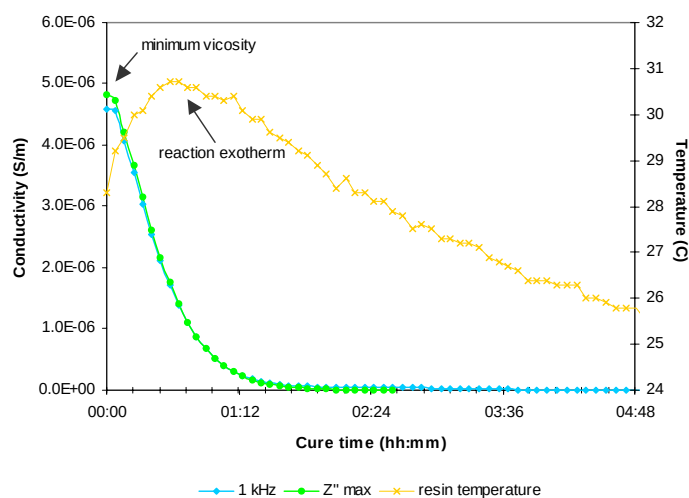


Figure 4.24 - Independently determined Z'' max and 1 kHz conductivity results for DP 460 cure.

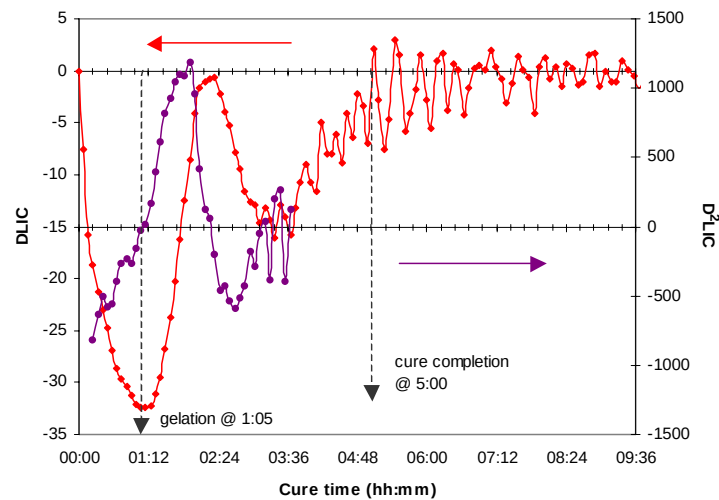


Figure 4.25 - Time derivatives of log conductivity showing important stages during cure of DP 460.

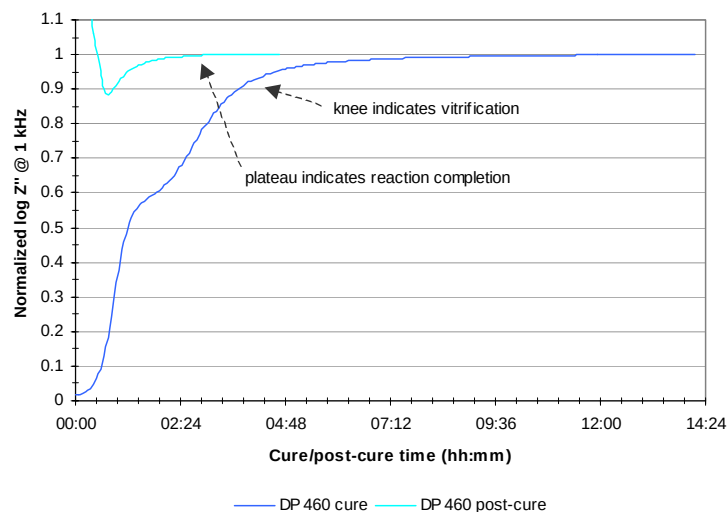


Figure 4.26 - Normalized imaginary impedance data for DP 460 cure and post-cure.

The results of the 1 kHz conductivity analysis for several of the materials are compared in Table 4.2. Here, the dielectric results compare well with information independently provided by material suppliers, indicating that the features used for timing different stages of the cure progression are suitable. The level of minimum conductivity after cure does not correspond to the

degree of cure merely to the completion of the cure reaction at that temperature. Further cure may still be possible at higher temperatures.

Table 4.2 - Detailed cure information using dielectric cure monitoring.

<i>measured data</i>	fresh SPSE90	aged SPSE90	HexPly 924	DP 460	DP 460 post-cure	SPSE84	SPSE84 post-cure	HexPly 913	unfilled XD 4601
minimum viscosity time (hh:mm)	1:30	1:25	1:15	0:00	n/a	0:50	n/a	1:03	0:22
minimum viscosity temperature (°C)	103	102	140	n/a	n/a	62	n/a	114	156
conductivity @ min viscosity (S/m)	3.0×10^{-5}	2.2×10^{-5}	1.8×10^{-4}	4.6×10^{-6}	n/a	2.7×10^{-2}	n/a	1.6×10^{-4}	2.4×10^{-4}
gelation time (hh:mm)	1:45	1:40	1:40	1:05	n/a	1:12	n/a	1:10	0:25
cure time (hh:mm)	2:50	3:10	3:20	5:00	3:20	2:40	3:15	2:25	1:00
conductivity @ cure end (S/m)	1.6×10^{-8}	7.4×10^{-8}	2.6×10^{-8}	4.3×10^{-9}	1.1×10^{-7}	2.2×10^{-2}	3.7×10^{-3}	1.5×10^{-8}	3.3×10^{-6}
<i>manufacturer's data</i>									
minimum viscosity temperature (°C)	105		150	n/a	n/a	98	n/a	122	n/a
gelation time (hh:mm)	n/a		1:30	1:00	n/a	n/a	n/a	1:30 (0:10 @ 125°C)	n/a
cure time (hh:mm)	3:00 (1:10 @ 110°C)		3:20 (2:00 @ 180°C)	24:00	1:50 (1:00 @ 100°C)	3:30 (1:30 @ 110°C)	n/a	2:20 (1:00 @ 125°C)	1:05 (1:00 @ 180°C)

Further plots in Figures 4.27 – 4.31 show the technique has sufficient sensitivity to successfully detect cure stages in a wide range of materials including high temperature processes, as well as material post-curing and shelf ageing. Whilst data was successfully obtained for the bulk XD4601 resin, no data could be determined for the metal particulate filled resin. This filled material showed no discernable peaks in either ε'' or Z'' , thought likely to be due to the effect of metal particles infiltrating the protective fabric layers covering the electrodes and short circuiting the cell.

The DP 460 data in Figure 4.24 shows a typical cure curve for a room temperature curing system. The system is liquid at room temperature and so the viscosity is a minimum at the outset, indicated by the conductivity maximum. As the reaction proceeds, indicated by the exotherm in the corresponding temperature data, the viscosity and hence the conductivity drops until no further reaction occurs and the conductivity shows no further change. This is the point at which there is no further change in the measured conductivity or where the time derivative of the log ion conductivity (DLIC) is zero, as indicated in Figure 4.25. The gel point is found from the inflexion

point in the conductivity with time trace or more simply, where DLIC is a minimum and the second time derivative of the log ion conductivity (D^2LIC) is zero.

Figure 4.27 shows the conductivity data for post-curing DP 460. This showed a drop in conductivity with time suggesting that further charged species movement was hindered by increased cross-links or by integration into the polymer network, thus a plateau in conductivity would correspond to vitrification at the higher post-cure temperature.

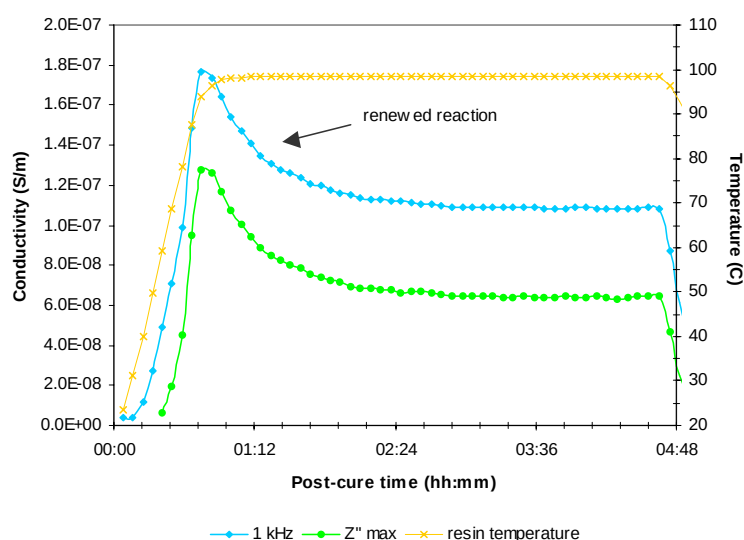


Figure 4.27 - Conductivity profiles of DP 460 during post-cure.

Differences in the electrical behaviour of the fresh and shelf-aged SPSE90, shown in Figure 4.28, can be similarly attributed to the mobility of charged species. As the material is heated the viscosity drops until the minimum is reached and the cure reaction begins. The minimum viscosity is reached sooner and the conductivity is lower for the aged material, indicating a higher minimum viscosity and less resin flow. Gelation occurs earlier and cure times are longer for the shelf-aged material, as might be expected. The conductivity of the aged material is higher at cure completion, possibly due to charged species being free to move relatively unimpeded by the network formed and a lower level of cure being achieved.

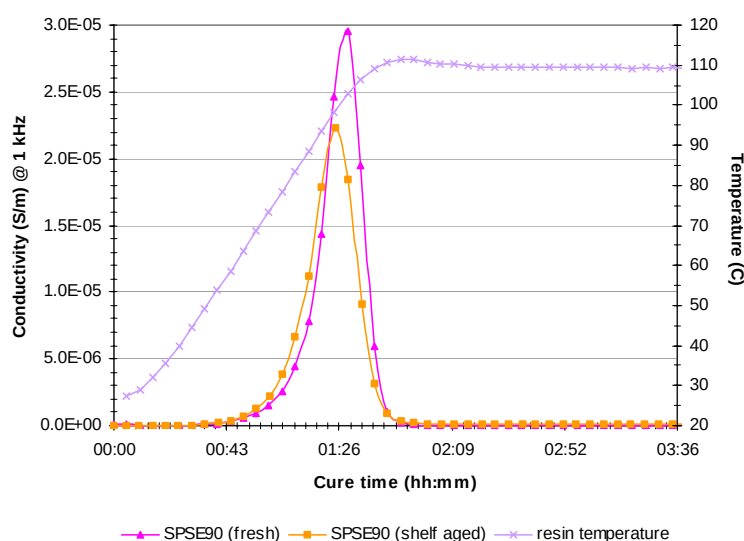


Figure 4.28 - Different cure conductivity profiles for fresh and shelf-aged SPSE90.

Similarly, glass composite pre-pregs Hexply 913 and very high temperature cure Hexply 924 also exhibited typical cure conductivity curves and could be successfully monitored using dielectric measurements. This can be seen in Figure 4.29.

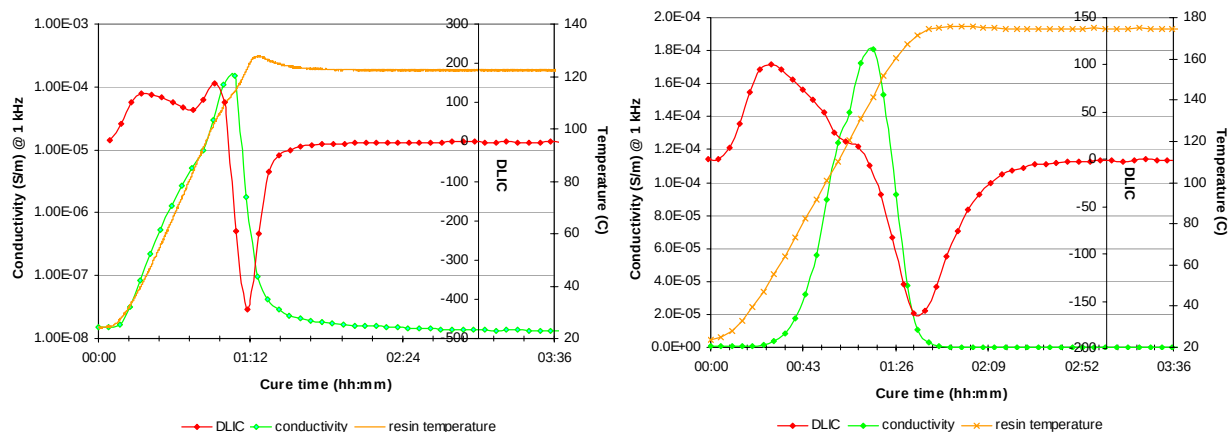


Figure 4.29 - Conductivity and time derivative of conductivity with cure for HexPly 913 glass (left) and HexPly 924 glass (right).

The high temperature curing XD4601 was very highly exothermic, as demonstrated in Figure 4.30. The viscosity/conductivity trace peaks before

the maximum resin temperature is reached, showing the reaction is well underway by that point, in fact the bulk of the reaction is over by the time the exotherm diminishes.

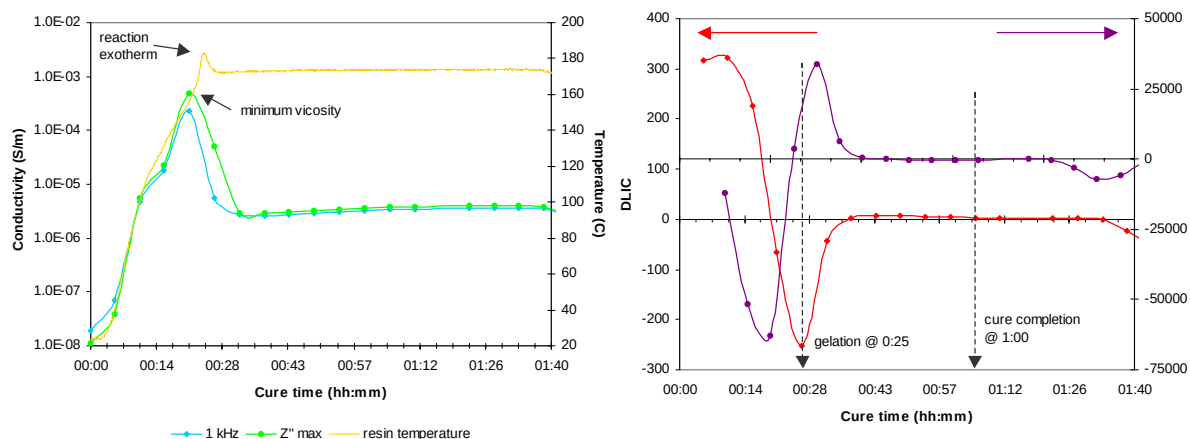


Figure 4.30 - Conductivity profiles for cure of unfilled XD4601 (left) and time derivatives of log conductivity showing the important stages during cure (right).

The conductivity profiles in Figure 4.31 were determined for SPSE84 with conductive carbon fibre reinforcement. This clearly demonstrates that materials containing conductive fillers can be accommodated for dielectric cure monitoring by introducing a barrier or filter between the sensor and surrounding resin.

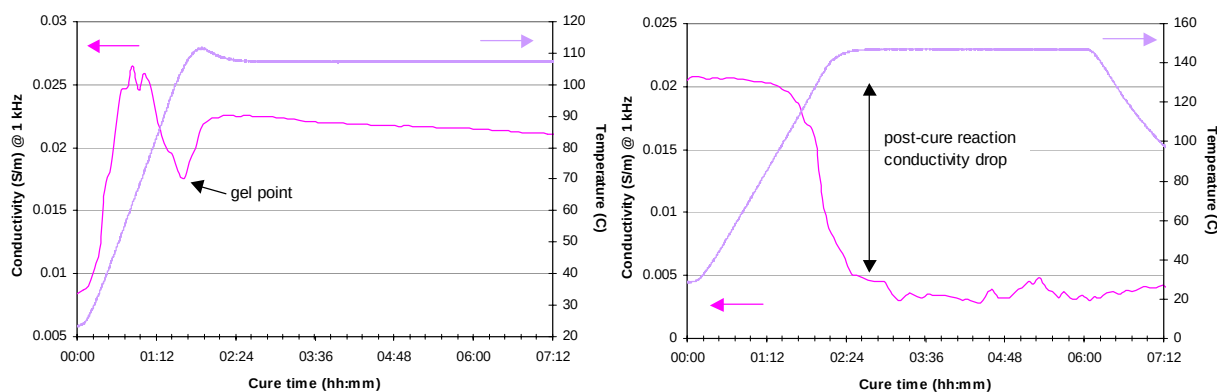


Figure 4.31 - Conductivity profiles for cure (left) and post-cure (right) of SPSE84 carbon.

This material displayed relaxation behaviour, indicated by the peaks in ϵ'' data exhibited. However, these peaks proved difficult to analyse using the various dielectric permittivity routes. These problems may be either due to the conductive nature of the reinforcement or the intrinsic nature of the resin,

which can be confirmed with unreinforced resin trials. These experiments were therefore analysed using the 1 kHz resin conductivity data. The cure results are more complex than previously seen, with a step change drop in the conductivity after the minimum viscosity but before cure completion, the cause of which is unclear. This more complex conductivity curve could be due to the creation of charged species as a result of the cure reaction rather than their integration into or restricted motion due to the polymer network, thus dielectric analysis is more difficult for this material.

The post-cure conductivity results are much more conclusive. These show a clear drop in conductivity as the higher post-cure temperature initiates further reaction, beyond the previous level achieved during the preliminary cure stage.

Notes:

- Although parallel plate sensors offer an average measure of cure through a material; the overlapping areas, alignment and separation of the two electrodes must be tightly controlled for valid results.
- Usually a thin layer of glass fibre fabric, polyimide film or thin porous PTFE peel ply is sufficient to protect electrodes from shorting due to contact with conductive fillers.
- The impedance frequency sweep time must be short enough that the curing system does not change appreciably during the measurement and can thus be considered instantaneous.
- Low applied voltages are required to minimise possible electrochemical reactions.
- Rubbers can exhibit very small dielectric changes with cure which can make them difficult to monitor via this route.
- Most commercial impedance/dielectric analysers are functionally equivalent and so can be used interchangeably.
- Condensation reactions (water produced as a by-product) can be problematic as conductive species are produced rather than removed which can complicate conductivity data.
- Higher applied voltages, larger sensor areas and wider inter-digitate spacing increase the field penetration.

- Temperature resistant sensors are required for high temperature applications and may need to be corrected for intrinsic temperature response.
- For high pressure applications, specialised sensors are available, many of which are designed to be permanent and re-usable, and can be built into tool walls.

4.5 Fibre Optic Strain Sensing

Some preliminary experiments were run using suitable fibres to check:

- the true wavelength-temperature sensitive factor, β (literature value of β is $6.65 \times 10^{-6} / ^\circ\text{C}$), and
- determine the noise limited strain resolution.

The fibre was subjected to three separate heating cycles:

- $2 ^\circ\text{C}/\text{min}$ to $115 ^\circ\text{C}$ followed by natural fan-assisted cooling,
- $5 ^\circ\text{C}$ steps to $100 ^\circ\text{C}$, 30 min dwell per step, and
- constant $30 ^\circ\text{C}$.

These were performed using a freely supported fibre Bragg grating, as shown in Figure 4.32, placed inside a programmable oven. A 2×2.3 mm thin film platinum resistance thermometer (PRT) was mounted in a 4-wire bridge configuration adjacent to the grating to monitor the local temperature.

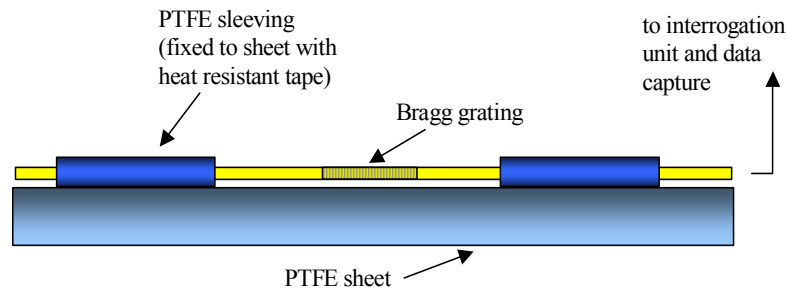


Figure 4.32 - Set-up for determining β coefficient and strain noise.

The specifications for the fibres and Bragg gratings used in this exercise were:

- Corning SMF 28 fibre - 6 mol% GeO doped silica core,
- centre wavelength 1306 - 1308 nm,
- grating length 12 mm,
- reflectivity $>90\%$,
- reflected spectrum FWHM <0.3 nm,

- standard bare fibre 9 μm core, 125 μm cladding and 250 μm acrylate recoated,
- 0.5 m pigtails (fibre lengths either side of the grating),
- nominal K of 0.805 /strain,
- nominal α_Λ of $0.55 \times 10^{-6} /^\circ\text{C}$, and
- nominal ζ of $6.1 \times 10^{-6} /^\circ\text{C}$.

Individual fibres were prepared by attaching to single-mode fibre patchcords with integrated angled-face APC-style end-connectors, using an arc fusion auto-splicer. Fibre ends were stripped, cleaned and cleaved flat for subsequent joining. The fused area was then protected with a heat-shrink metal reinforced support. Connector surfaces were kept covered when not in use to protect them from deleterious scratches and dirt.

An ElectroPhotonics Corporation FLS 3100 interrogation module was used to illuminate the Bragg grating and to monitor the reflected wavelength via the fibre end-connector. Equations, supplied with the unit calibration certificate, were used to convert the output voltage response into the corresponding wavelength. The signal was subsequently displayed and collected in real-time via a data acquisition card.

The dynamic heating cycle resulted in a temperature lag between the instantaneous oven temperature, as measured by the PRT, and the internal fibre temperature. This was demonstrated by the displacement between the heating and cooling portions of the cycle, as shown by the graph in Figure 4.33. Taking an average of the heating and cooling slopes gives an estimate of $6.844 \times 10^{-6} /^\circ\text{C}$ for β .

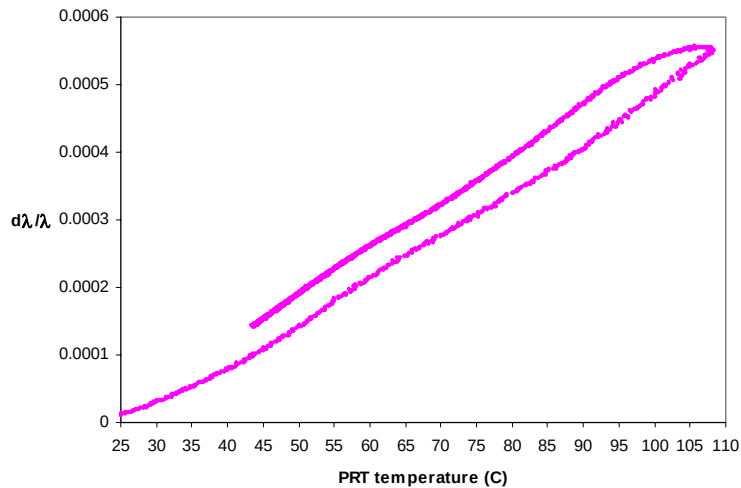


Figure 4.33 - Bragg response to ramped heating and cooling.

The staggered heating cycle was designed to ensure thermal equilibrium was achieved. This was verified by the wavelength plateaus shown in Figure 4.34. Averaging the wavelength and temperature data of the plateaus enabled the β coefficient to be calculated, as shown in Figure 4.35, giving a value of $6.831 \times 10^{-6} / ^\circ\text{C}$.

This final value was used for all subsequent temperature corrections to the Bragg wavelength.

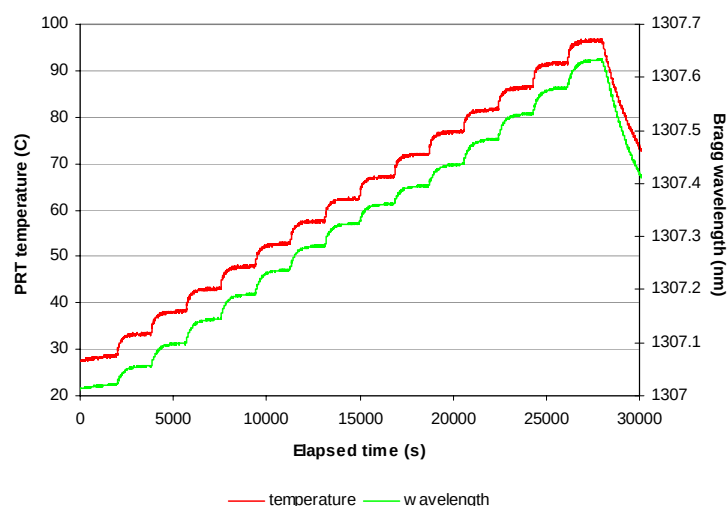


Figure 4.34 - PRT temperature and Bragg wavelength response to stepped heating.

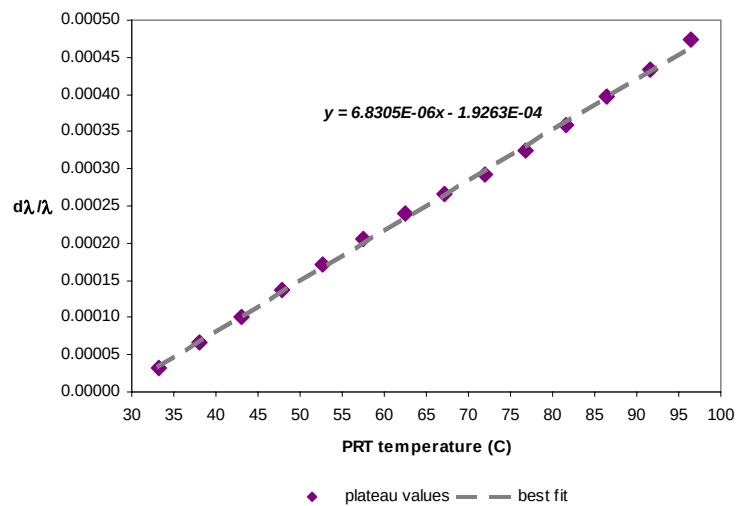


Figure 4.35 - Plot of plateau values of both wavelength and temperature for β evaluation.

Small fluctuations in temperature and wavelength were observed during the constant temperature cycle. Following wavelength corrections due to temperature variation, the minimum practical strain resolution was found to be around 2 μ strain, as shown in Figure 4.36.

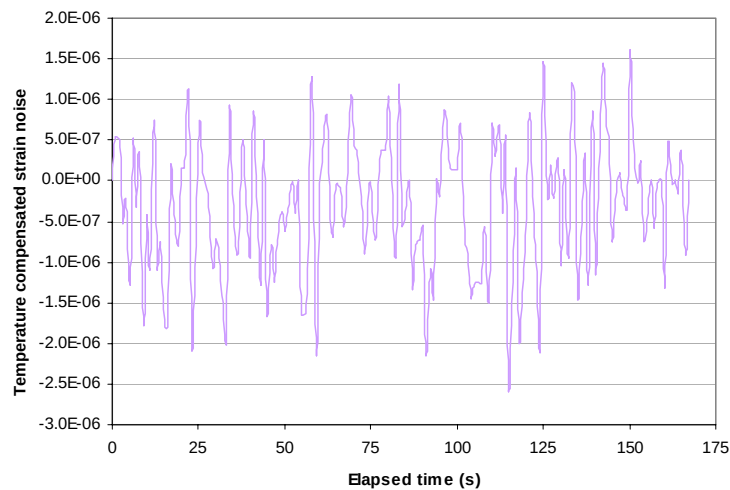


Figure 4.36 - Typical fibre Bragg grating strain noise.

Subsequent cure monitoring tests were carried out on a diverse range of materials, listed in Table 4.3. Tests carried out on composite pre-pregs were manufactured by laying up the required number of plies thickness with fibre Bragg gratings included on the mid-plane. Sections were cut-out from the central plies to accommodate narrow bore PTFE tubing, used to protect the fibre where it exits the material. An example of this arrangement is shown in Figure 4.37, both real and schematic.

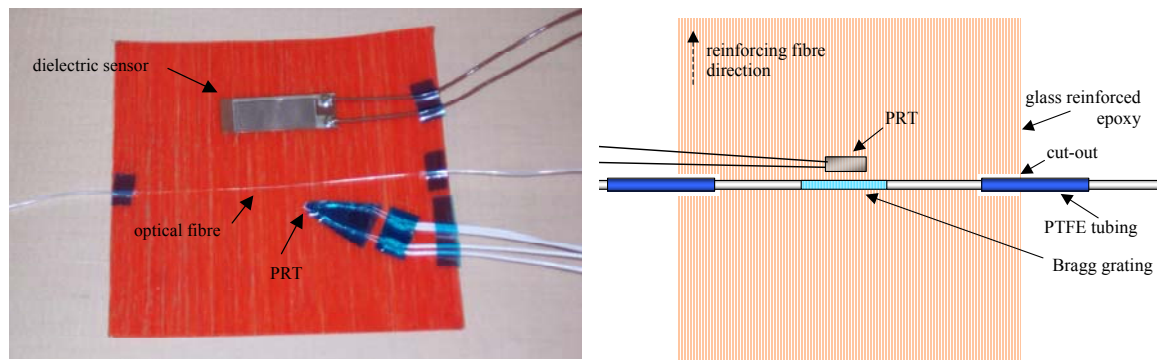


Figure 4.37 - Mechanism for fibre inclusion, shown for 90° orientation.

Table 4.3 - Materials and cure profiles used in fibre optic strain cure monitoring study.

Material	Format	Cure Cycle
Hexcel Composites HexPly 913 ud glass/epoxy pre-preg - 0° & 90° orientation - in-date & out-of-date	composite laminate 20 plies thick	2 °C/min 120-125 °C 4 hour dwell
3M Scotch-Weld DP 460 epoxy adhesive - cure & post-cure	bulk resin plaque	25 °C > 12 hour dwell
		1 °C/min 100 °C 4 hour dwell
Dow Chemicals XD 4601 epoxy adhesive - cure & extra heating cycles	bulk resin plaque	30 °C/min 180 °C 2 hour dwell
		5 °C/min 200 °C no dwell
SP Systems SPSE84 ud carbon/epoxy pre-preg - cure & post-cure	composite laminate 14 plies thick	1 °C/min 110 °C 6 hour dwell
		1 °C/min 150 °C 4 hour dwell

The resulting laminates were vacuum consolidated as shown in Figure 4.38 and cured. For bulk resin samples, the moulds were filled with liquid resin and the fibre Bragg grating laid into the central region. A PRT was positioned close to the grating in both cases to allow for accurate temperature correction.

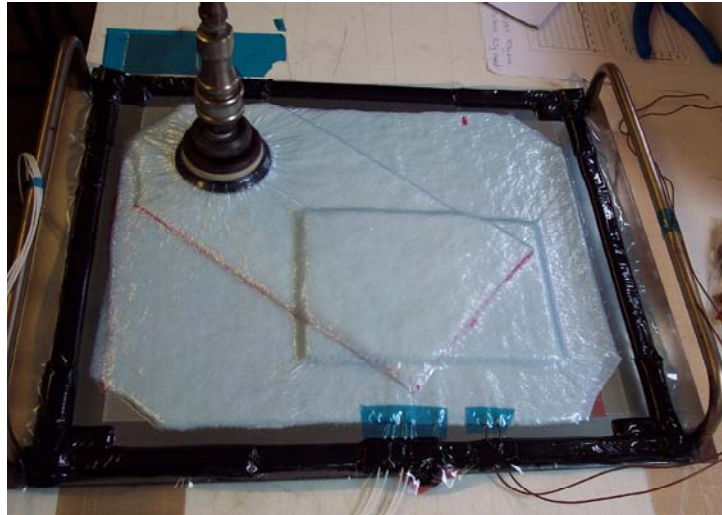


Figure 4.38 - Typical vacuum bagging/consolidation of test laminates.

Results from the initial fibre Bragg grating tests on the effects of grating orientation are presented in Figures 4.39 and 4.40. These show that compressive strain changes are observed close to 120 °C which are likely to be related to cure shrinkage. Dramatically greater strain changes are seen in the 90° as compared with the 0° direction due to restrictions on the cure shrinkage imposed by the fibre reinforcement. The strain changes occur between 1 hr 12 mins and 2hr 24 mins for the 90° orientation, the change in strain slowing with time eventually reaching a plateau, as the cure reaction and the shrinkage it causes diminishes. The changes in strain seen prior to cure shrinkage are possibly due to fibre optic relaxation and/or changes in material thermal expansion and viscosity, but are unlikely to be cure related.

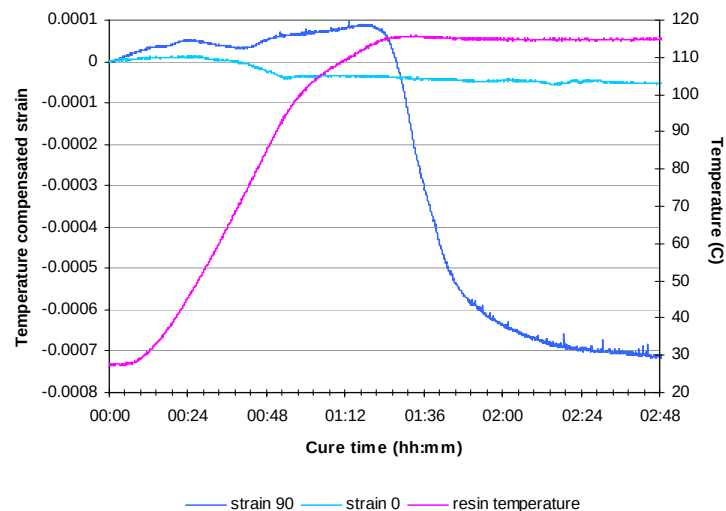


Figure 4.39 - Plot of temperature and strain with time for both 0° and 90° Bragg gratings.

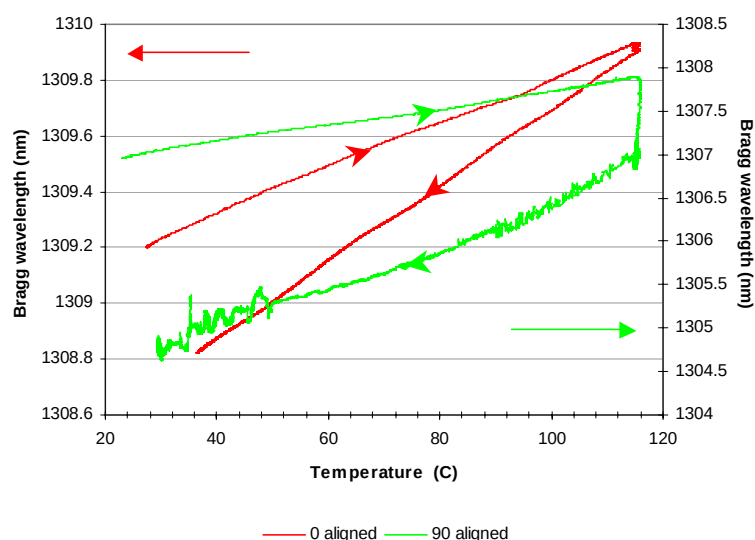


Figure 4.40 - Plot of Bragg wavelength with temperature for 0° and 90° Bragg gratings.

Results from the tests investigating the sensitivity of strain measurements to material age are shown in Figures 4.41 and 4.42. These show there is a large relaxation of the pre-tension strain in the optic fibre which is relieved as the resin viscosity drops with rising temperature. The aged material is expected to have undergone a measure of cure reaction before being subjected to the cure cycle, a theory supported by the lesser accumulation of cure shrinkage and the earlier cure completion. This may also indicate a lower degree of cure in the aged material, which is frequently associated material ageing.

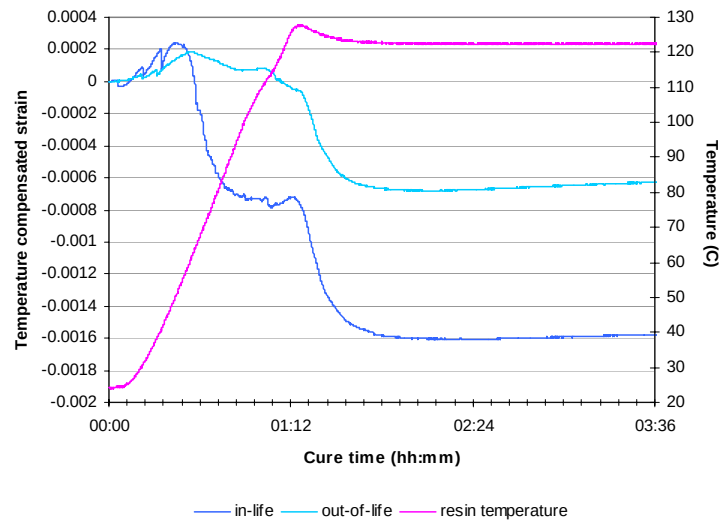


Figure 4.41 - Plot of temperature and strain with time for both in-life and out-of-date Hexply 913 glass.

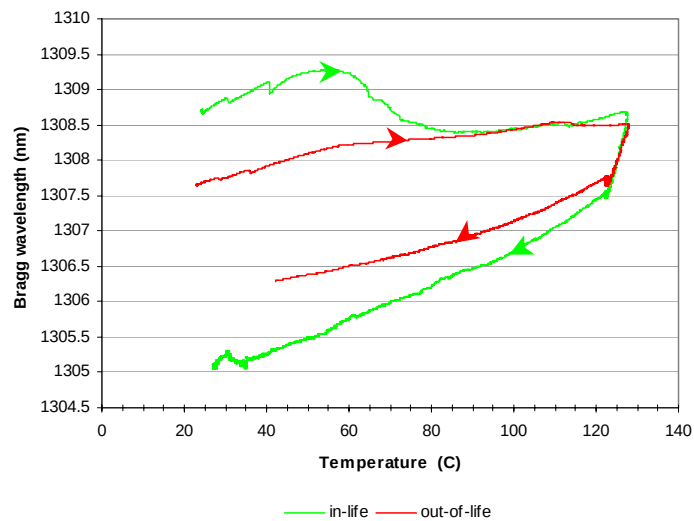


Figure 4.42 - Plot of Bragg wavelength with temperature for in-life and out-of-date Hexply 913 glass.

The technique has good repeatability, shown for the identical material/set-up from the 90° data in Figure 4.39 and the in-life data in Figure 4.41 which display similar shrinkages, as measured from the gel point, of ~ 0.0008 compressive strain.

The strain data from the SPSE84 carbon material is shown in Figures 4.43 – 4.45. Figure 4.43 shows the cure data where the gel point and end of cure plateau can be readily distinguished. The relaxation of the fibre pre-tension and the cure shrinkage can also be clearly seen.

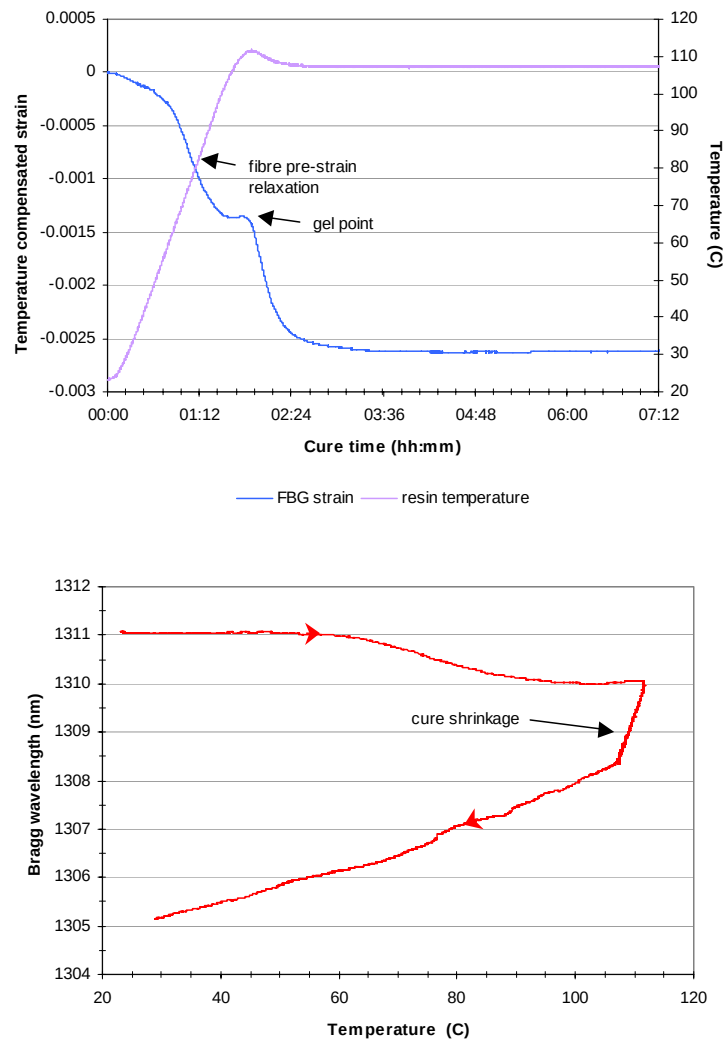


Figure 4.43 - Fibre Bragg cure monitoring of SPSE84 carbon: shrinkage strain with time (upper) and Bragg wavelength with temperature changes (lower).

Figure 4.44, at first glance, suggests the strain method has very little sensitivity to post-cure reaction. However, by magnifying the initial data, it can be seen in Figure 4.45 that although extremely small there is a definite continued reaction at the post-cure dwell temperature.

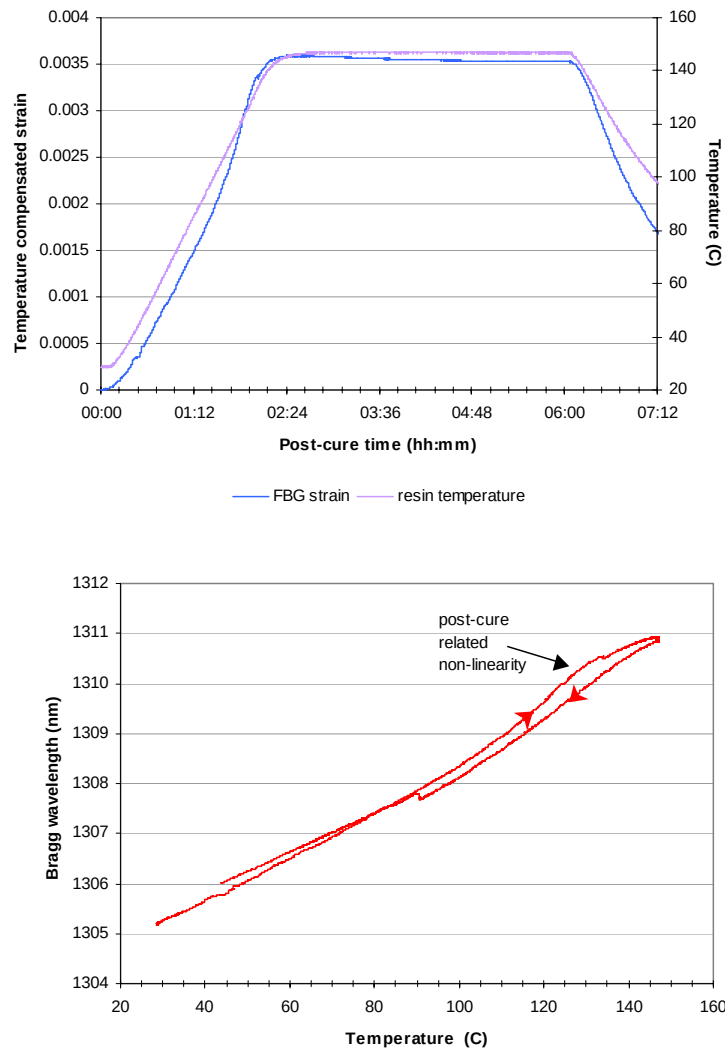


Figure 4.44 - Fibre Bragg post-cure monitoring of SPSE84 carbon: shrinkage strain with time (upper) and Bragg wavelength with temperature changes (lower).

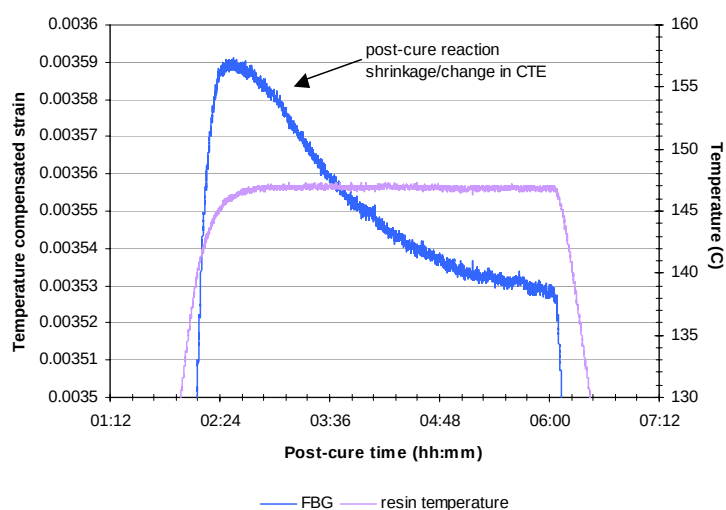


Figure 4.45 - Magnified view of fibre Bragg SPSE84 carbon post-cure monitoring data.

The unreinforced resins show similar characteristic strain traces, as presented in Figures 4.46 - 4.48.

Figure 4.46 shows the strain data with cure time for the DP 460. This shows a characteristic cure shrinkage trace and a typical reaction exotherm.

Inspecting the initial cure region in greater detail, initially little or no strain is apparent whilst the viscosity of the liquid adhesive is low and the optical fibre is unconstrained, giving a zero strain plateau. As the viscosity of the resin increases and the gel point is reached, stress transfer between the adhesive and the fibre occurs. At this point, the fibre becomes constrained and responds to changes in both the thermal expansion and shrinkage of the adhesive resin. This combination of increased shrinkage and the higher coefficient of thermal expansion (CTE) of the surrounding material creates a discrepancy in the temperature compensation and the strain deviates from the zero level. The final plateau indicates the end of the shrinkage and the eventual vitrification of the system.

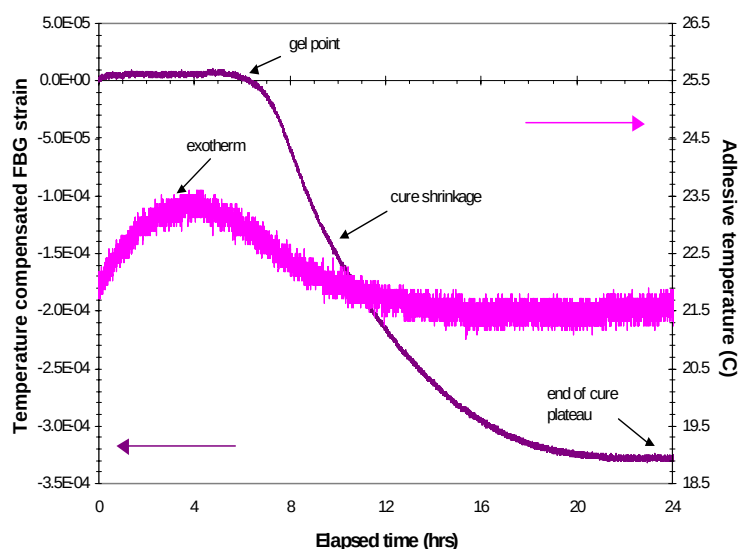


Figure 4.46 - Strain cure monitoring of DP 460.

Figure 4.47 shows the cure shrinkage results for high temperature curing XD4601. This material exhibits a severely exothermic cure reaction. Closer inspection of the data shows that before the temperature spike occurs, the temperature of the material deviates from its linear increase towards the set cure temperature. This could well indicate a significant level of cure reaction beginning to take place. There are no other features during the dwell period suggesting that cure is completed before the sample reaches the constant dwell temperature.

The onset of gelation can be seen more clearly in Figure 4.48 (upper). Since the temperature spike coincides with the cure shrinkage stage, it acts to camouflage the expected compressive strain, but the gel point can be determined from the point of deviation of the strain from its initial zero plateau position.

On cooling, a transition temperature is reached, 110 °C, where the CTE of the adhesive increases dramatically. This is related to the glass transition temperature, demonstrating a marked change in the adhesive CTE from the rubbery to glassy states.

Subsequent heating cycles are seen in Figure 4.48 (centre) and (lower). The first heating cycle showed that on heating, there was a sudden drop in tensile strain. This is likely to be a strain relaxation which occurred on reaching the

glass transition temperature of the adhesive material as there is no evidence of its reoccurrence on later cycles. This glass transition temperature in turn shows some progression with continued thermal cycling, increasing from 110 °C to 115 °C and finally to 120 °C.

It can also be noted from these plots that the CTE of the adhesive is markedly non-linear.

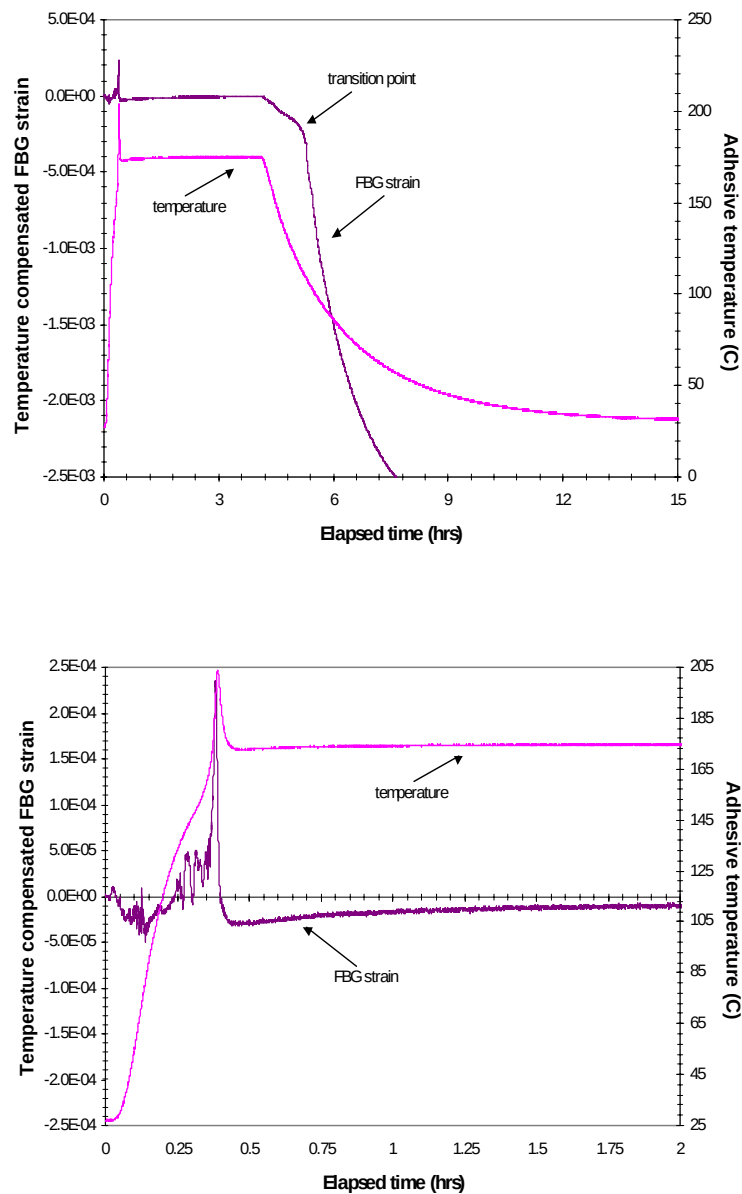


Figure 4.47 - Strain cure monitoring of XD 4601: heating, dwell and cooling stages (upper) and initial cure region magnified (lower).

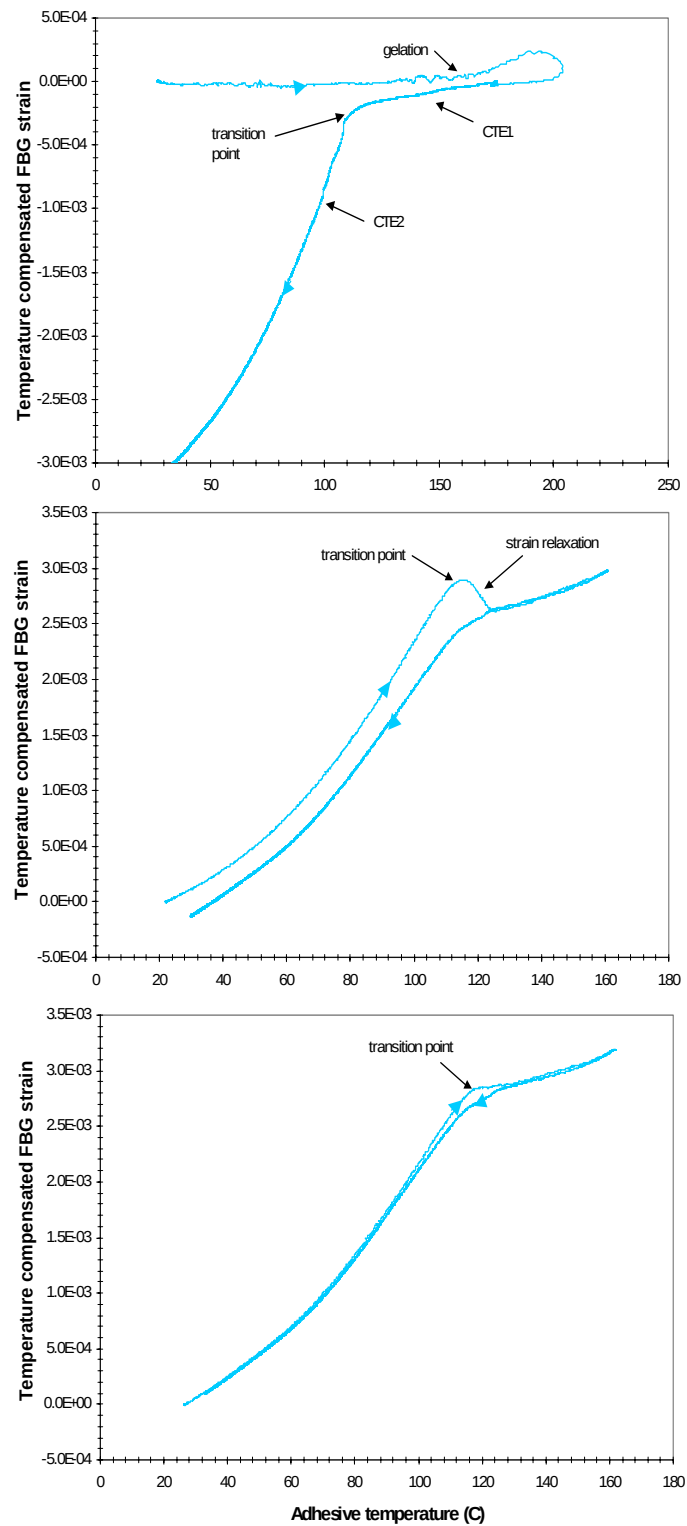


Figure 4.48 - Strain changes with temperature for XD 4601: during cure (upper), and subsequent additional heating cycles (centre and lower).

The fibre Bragg grating strain cure results are summarised in Table 4.4. These show good correlation between the values determined using strain monitoring and those from dielectric analysis (Table 4.2).

Table 4.4 - Detailed cure information from the cure strain study.

	SPSE84	post-cure SPSE84	HexPly 913	DP 460	XD 4601
<i>test data</i>					
gelation time (hh:mm)	1:45	n/a	1:12	6:00	0:20
cure time (hh:mm)	3:45	plateau not reached	2:00	~24:00	1:00
<i>manufacturer's data</i>					
gelation time (hh:mm)	n/a	n/a	1:30 (0:10 @ 125°C)	n/a	n/a
cure time (hh:mm)	3:30 (1:30 @ 110°C)	n/a	2:20 (1:00 @ 125°C)	1:50 (1:00 @ 100°C)	1:05 (1:00@180°C)

Notes:

- Fibre Bragg strain sensing is insensitive to cure shrinkage prior to gelation, as the material needs to be unable to flow for strain transfer to occur.
- Sensors have greater sensitivity to cure shrinkage when aligned perpendicular to the principal reinforcement direction.
- Sensible precautions should be taken to ensure that neither the resin constituents nor the processing conditions are deleterious to the optical fibre.
- Fibre pre-tension, bends and applied vacuum/compaction pressure all act to complicate the cure shrinkage strain profile.
- Fibre optic sensors are very fragile, especially at the point at which they exit the material due to the stiffness mismatch and require reinforcement in this region.

- Tight radii of curvature in fibre optics result in signal loss and are best avoided.
- Bragg gratings can be located along a length of fibre optic by their enhanced colouration and increased surface roughness.
- For the most accurate measurements, β should be measured independently for each fibre.
- Pressure/vacuum also affects the Bragg wavelength, although the effect on the resin is likely to be far greater than that on the grating.
- Large strain changes, particularly at room temperature where the temperature does not counteract the change in wavelength with shrinkage, can cause the fibre signal to go “out of range” which can lead to false interpretations.
- The monitored region can be extended by using multiple fibres or by interrogating in turn several gratings on a single length of optical fibre.

5 Industrial Demonstrations

5.1 Ultrasonic Industrial Case Study

This case study describes the application of ultrasonic cure monitoring to a continuous manufacturing process for vinyl flooring. The rolls of flooring material are typically a few metres wide and up to a few hundred metres long.

The flooring was measured in through-transmission. The ultrasonic probes were directly in contact with opposite sides of the material, with the ultrasound pulse making a single pass through.

Before the on-site industrial trial, preparatory work at NPL confirmed that it was possible to transmit a satisfactory ultrasonic signal through typical flooring materials, so reducing the scope for technical problems such as excessive attenuation or signal scatter during the trial, see Figures 5.1 and 5.2.

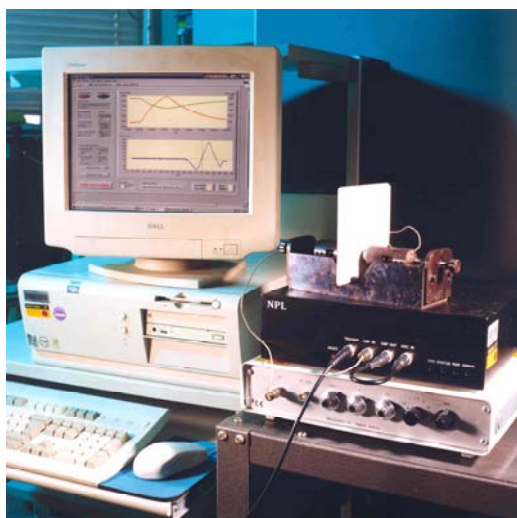


Figure 5.1 - Typical laboratory ultrasonic measurement set-up.

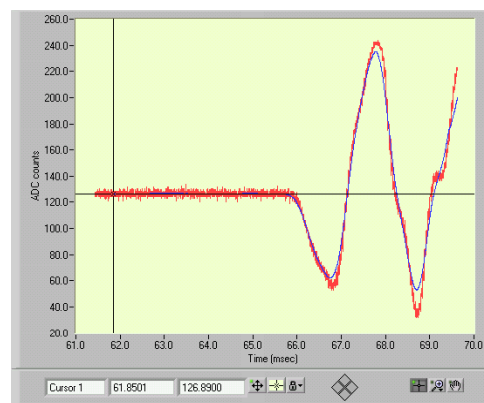


Figure 5.2 - Typical flooring ultrasonic signal.

During the industrial trial on the flooring production line, the following issues were investigated:

- Variation of ultrasonic velocity with line speed and roll position.
- Degree of correlation between in-line ultrasonic tests and current QA physical property tests.

The flooring is produced from a PVC plastisol material which is impregnated onto a supporting fabric. The process is a continuous production line where the impregnated fabric is passed through several coating and patterning stages and through hot ovens to gel the flooring into the final product.

It can be seen from Figure 5.3 that in-line tests revealed a line speed, i.e. 8 m/s, that gave the most consistent values of ultrasonic velocity. As ultrasonic velocity is related to degree-of-cure, this line speed is optimum for producing a material that is cured uniformly across the entire width of the production line.

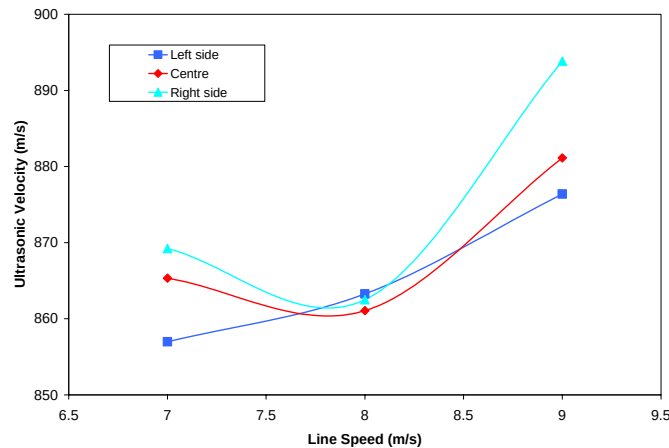


Figure 5.3 - Results of ultrasonic tests at three positions across the flooring width produced at different process speeds.

Although no direct correlation was found with the selection of physical property tests as conducted post-manufacture, it was discovered that QA test failures were most often caused by over-cure of the material. As a result, optimising the process would bring about simultaneous savings on the processing cycle time as well as improvements in product quality and durability.

5.2 Dielectric Industrial Case Study

This case study describes the application of dielectric cure monitoring to a press moulding process for various reinforced-plastic products.

The manufacture of a 1 m x 0.8 m side panel for a forklift truck, with a thickness of 4.5 mm was studied. Fabrication was in a pre-heated mould tool using a fast curing glass/polyester low pressure moulding compound at a pressure of only 1.5 MPa. Here, a high quality surface finish is the most important outcome. Under-cure results in problems with de-moulding of parts and over-cure can cause unacceptable surface pitting. Previously, the company had based cure procedures purely on past experience.

Preliminary laboratory studies were conducted by University of Ulster to assess the suitability of the material to dielectric analysis and determine the appropriate a.c. frequency for cure sensitive measurements (in this case ~ 1 kHz) shown in Figure 5.4.

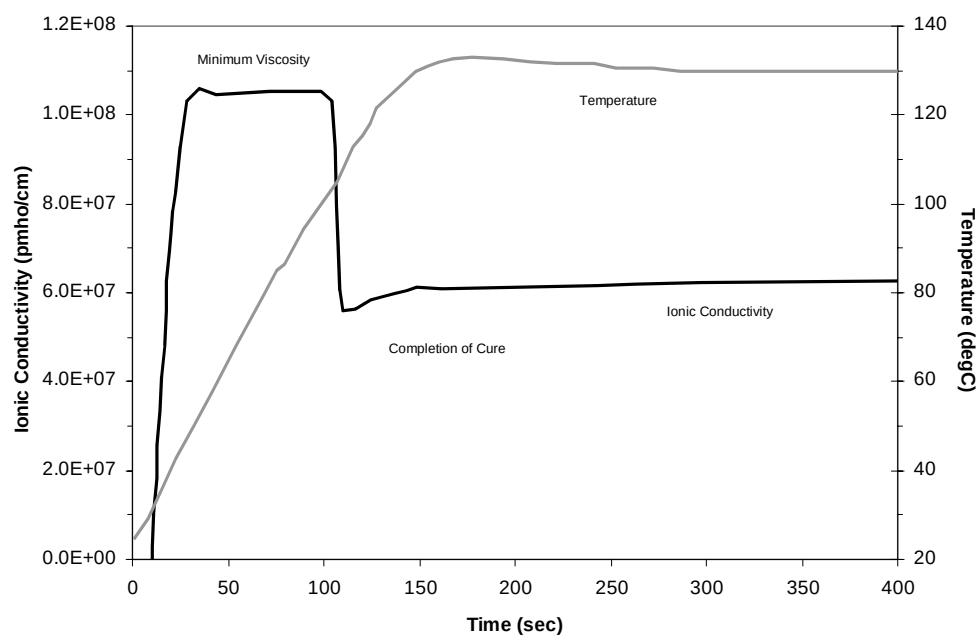


Figure 5.4 - Dielectric results from a ramped heating laboratory instrument at 130 °C and 1 kHz.

The preparatory work also confirmed that traditional methods, such as DSC or DMA were not directly representative of the process due to the initial temperature ramp applied to achieve the necessary process temperature, which can overshoot the target value; difficulties exacerbated by the fast curing behaviour of the system. This strongly indicated the need for in-situ measurements, such as demonstrated by the preliminary results shown in Figure 5.5.

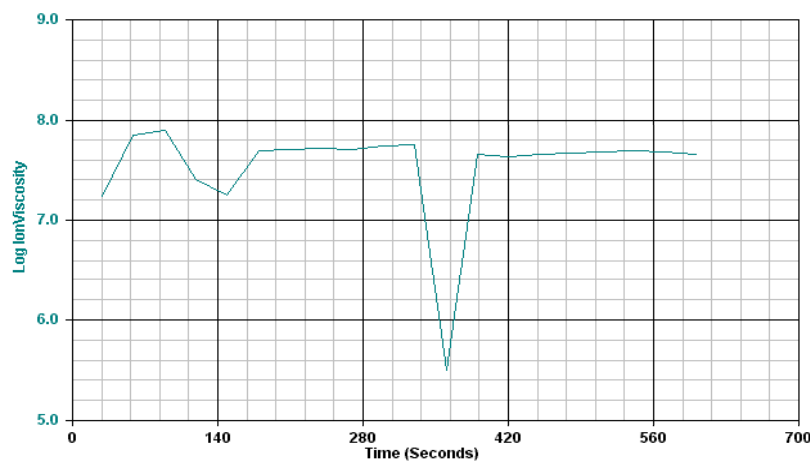


Figure 5.5 - LPMC dielectric results from laboratory platen press tests mimicking industrial process at 170 °C and 1 kHz.

The following issues were investigated during the industrial trials:

- Effect of mould temperature on cure, flow, cycle time and thus component quality.
- Different material formulations.
- Material ageing effects on cycle time and part quality.

The changing electrical properties of the material were measured using single surface inter-digitated electrode sensors, placed inside the pre-cut composite material, within the mould cavity.

The shear edge of the pilot tooling would slice sensor connections, so modifications were made by drilling two small paths through to the mould cavity to accommodate the dielectric and thermocouple sensor leads snugly. This granted sensor access but prevented material filling the channels. This pilot set-up is shown in Figure 5.6.



Figure 5.6 - Sensors positioned in material ‘charge’ inside modified pilot industrial tool.

Some of the results obtained from the pilot tool trial simulating the industrial process are presented in Figure 5.7 and summarised in Table 5.1. The effect of mould release agents, used to facilitate de-moulding of parts from the tool was ignored here, but in many cases this may have significant ramifications on the results obtained.

The results show that the standard material vitrifies after 220 s. In comparison, material shelf-aged within nominally acceptable limits shows a sharp minimum viscosity, with limited fill and flow time, before cure is completed after only 120 s.

Under-cured (115 °C) and slow cure formulation materials both exhibited long minimum viscosity periods and continued gradual cure reaction, even after 300 - 400 s.

Adopting process optimisation using dielectrics would produce savings by shortening cycle times, provide an opportunity for faster prototyping (process and product development, introduction of new materials) and reduce losses from product failures.

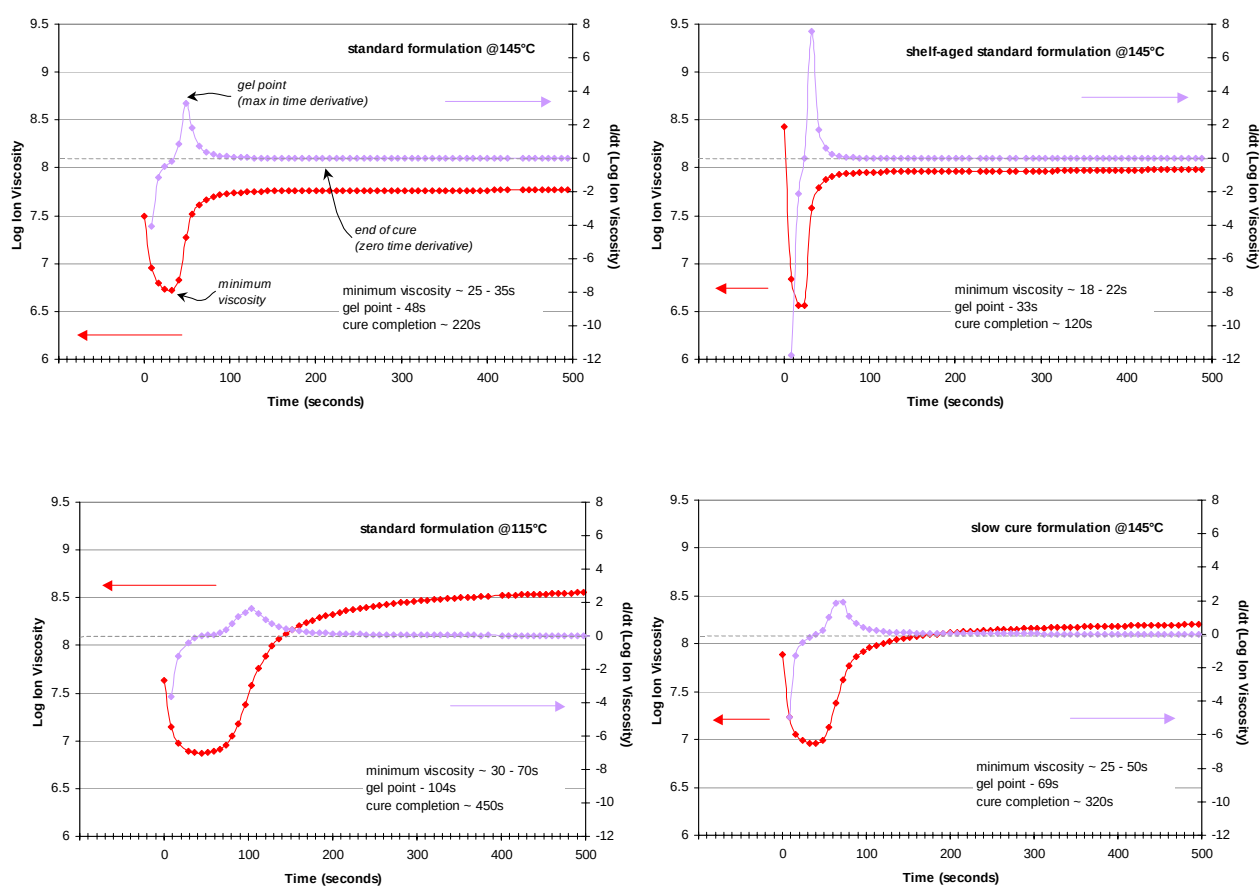


Figure 5.7 - Results of dielectric tests on different materials and at different temperatures, data represented as log ion viscosity and its time derivative.

Table 5.1 - Summary of critical process parameters and cure stage data from results of dielectric tests on different materials and at different temperatures.

Material	Cure Temperature (°C)	Time to Gel Point (s)	Time to End of Cure (s)
Standard LPMC	115	45	450
Standard LPMC	145	33	220
Shelf-aged Standard LPMC	145	24	120
Slow-cure LPMC formulation	145	39	320

5.3 Acoustic Industrial Case Study

This case study describes the application of acoustic cure monitoring to self-levelling specialist heavy duty industrial floor screeds produced in-situ.

Hygienic flooring, for the food, pharmaceutical and health industries, containing anti-bacterial agents was studied. The floor is mixed and laid in-situ over large areas where temperature and humidity are often uncontrollable. The period over which the area cannot be trafficked may be critical and costly for both customer and, as a result of severe time penalties, floor supplier. For this reason, accurate predictions and real-time information on the usability of the flooring is sometimes essential.

Broadband low frequency sound wave pulses are produced by a transducer and transmitted into the flooring through a solid rod waveguide in direct contact with the material. This signal travels horizontally along the flooring to the receiving transducer/waveguide combination, situated some distance away.

The received signal is monitored and the frequency corresponding to the peak amplitude is recorded from the resulting spectrum, examples shown in Figure 5.8. As the stiffness of the material changes, so the resonant frequency shifts also and a cure curve is produced.

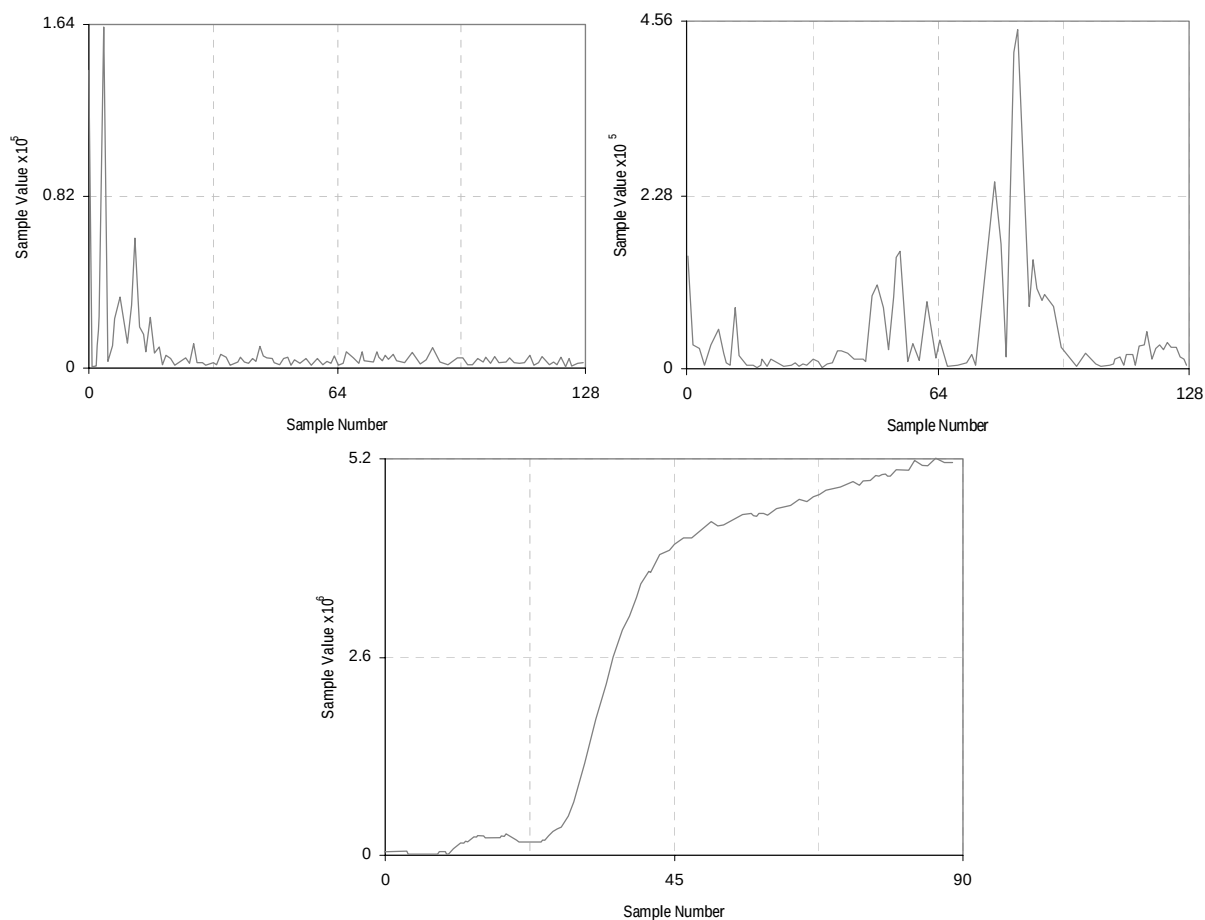


Figure 5.8 - Typical spectrum for uncured resin (top left), cured resin (top right) and the resulting cure curve with time (bottom).

The material mixture consists of a polyol emulsion resin base, a blended hardener (undesirable reactions from preferred low viscosity hardener are tempered by blending with favourably reacting hardener but with higher viscosity), mineral fillers and pigments. The ideal hardener blend would produce the cure curve shown in Figure 5.9.

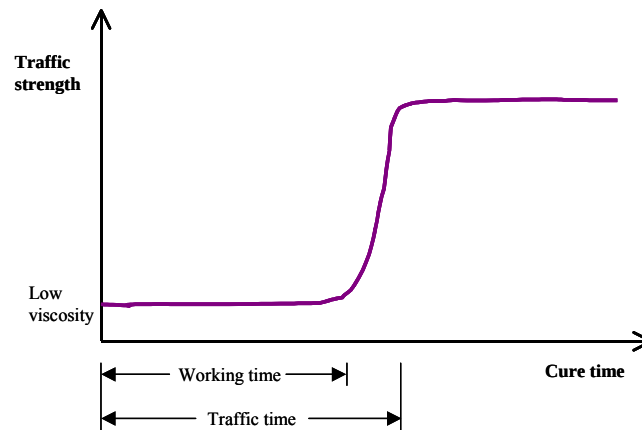


Figure 5.9 - Ideal cure curve for self-levelling flooring with long working time at low viscosity and quick cure to full strength.

Before the industrial scale field trial, some preliminary measurements were carried out by Testsure on laboratory sized samples. These results are presented in Figure 5.10.

As the flooring is a mixture of resin, hardener, cement, lime, pigment and aggregates, the curing process is a complex system of competing reactions, demonstrated by the multitude of peaks and troughs on the traces. Ideally, the flooring should have low viscosity initially, for as long as possible, to allow good self-levelling to occur (namely a long working time), followed by rapid conversion into a hard, load bearing surface.

Several formulations were investigated using different hardener blends. The results show:

- Formulations B and C, with lower viscosities, have reduced working times compared to benchmark formulation A.
- Formulations D, E and F, with higher viscosities, have greater working times compared to benchmark formulation A.

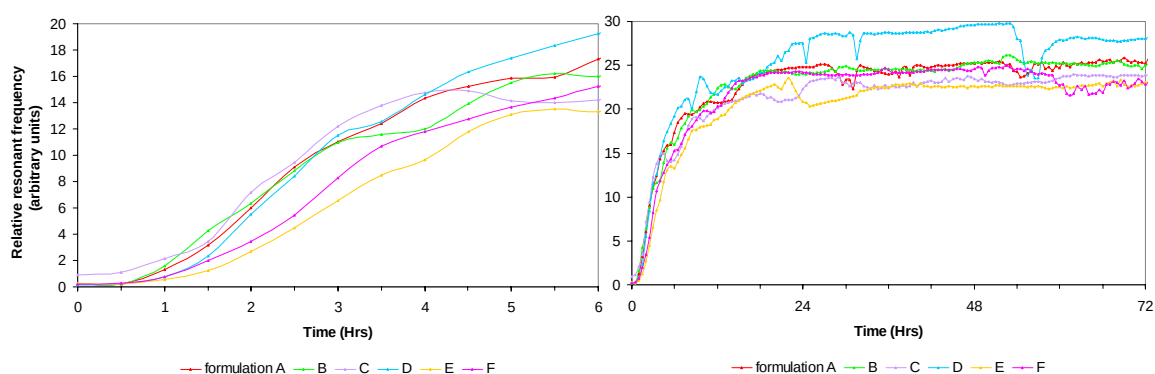


Figure 5.10 - Results of acoustic tests on flooring samples made with different viscosity/reactivity hardener formulations over periods of 6 hours (left) and 1 week (right).

The results obtained from the industrial field trial, which is pictured in Figure 5.11, are presented in Figure 5.12. This shows the difference in the characteristic cure profile for a nominally identical flooring compound laid under different conditions. The trial flooring exhibited markedly slower cure conversion and fewer anomalous features. This clearly demonstrates a need to appreciate the potential problems in extrapolating laboratory measurements directly to the field where scale and environmental factors are different.

Uncontrollable external temperature/humidity and mineral quality, varying thermal capacity of under floor materials and different surface area-to-volume ratios are all factors which make cure prediction difficult for this application and in-situ monitoring both valuable and cost effective, particularly for cases of extreme environmental conditions and in high value jobs.



Figure 5.11 - Typical set-up for field trial acoustic cure monitoring measurements.

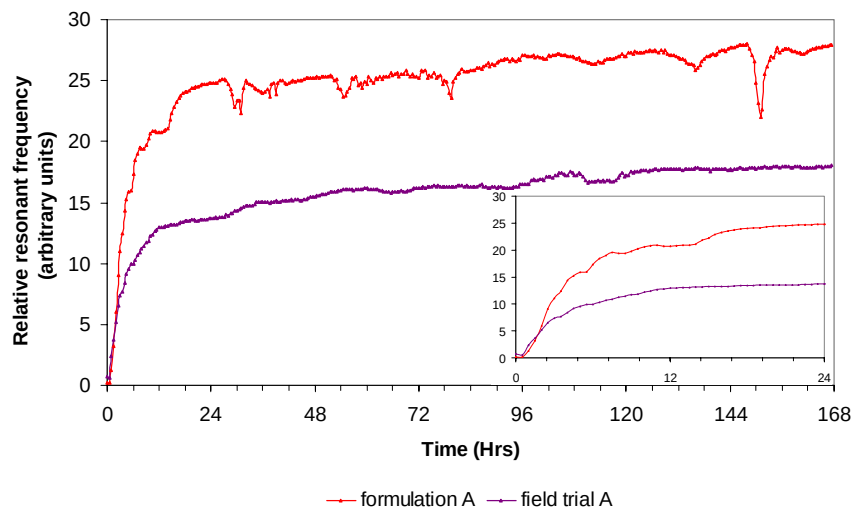


Figure 5.12 - Comparison of results from laboratory sized sample and scaled field trial for formulation A (inset: first 24 hours).

6 Summary/Conclusions

Tables 6.1, 6.2 and 6.3 present an overview of the important factors for the main cure monitoring techniques, required when making a selection. These are, respectively:

- important cure stages detected
- cost, contact and access
- process suitability.

Table 6.1 - Overview of cure characteristics detectable with the main monitoring techniques.

Method	Cure capability / sensitivity					
	<i>Resin fill</i>	<i>Minimum viscosity</i>	<i>Gel point</i>	<i>End of cure</i>	<i>Degree of cure</i>	<i>Other</i>
Temperature	×	×	×	✓	✓	reaction rate
Acoustic	✓	×	✓	✓	✓	
Ultrasonic	✓	×	✓	✓	✓	regression
Dielectric	✓	✓	✓	✓	✓	post-cure
Fibre Bragg	×	×	✓	✓	×	post-cure Tg CTE relaxations structural health

Table 6.2 - Overview of range of application issues for the main monitoring techniques.

Method	Spatial	Contact	Access	Cabling	Re-use	Sensor cost
Temperature	LOCAL/GLOBAL	Y / N	INT / EXT	Y / N	Y / N	£2 - £200
Acoustic	GLOBAL	Y	INT / EXT	Y	Y	£500
Ultrasonic	BULK	Y	EXT (1 or 2 sided)	Y	Y	£500
Dielectric	LOCAL / BULK	Y	INT / EXT	Y	Y / N	£2.50 - £2000
Fibre Bragg	LOCAL	Y	INT	Y	N	£100

Key:

Bulk = average measurement through-thickness

Local = small volume close to sensor

Global = area measurement

Re-use = reusability of sensors, whether or not they are disposable/embedded in part

Price ranges = lower (disposable/low tech option) to higher (re-usable/robust/bespoke/high tech option)

Table 6.3 - Overview of applicability to broad manufacturing processes of the main monitoring techniques.

Method	Process suitability		
	<i>Open process</i> e.g. paint coating	<i>Closed process</i> e.g. press moulding	<i>Continuous process</i> e.g. pultrusion
Temperature	all suitable	only contact methods (access ports required)	all suitable (cabling not ideal)
Acoustic	suitable	suitable (access ports required)	suitable (cabling not ideal)
Ultrasonic	one-sided access	all suitable (access ports required)	all suitable (cabling not ideal and transducers static)
Dielectric	all suitable	all suitable (in-mould sensors available or access ports required)	inter-digitated suitable only (cabling not ideal)
Fibre Bragg	suitable	suitable (access ports required)	suitable (fragility and cabling not ideal)

In general, despite some drawbacks in specific situations, it is better to know something, however limited, about the material being processed than nothing at all. As an absolute minimum, the material temperature should be measured independently of the programmed temperature such that any problems can be discovered and corrected quickly. As the simplest and most easily interpreted of all the monitoring methods discussed here, it can be tailored to suit all circumstances, providing either qualitative or quantitative data for comparison to the “ideal” product/process cycle.

Similarly, the two ultrasonic techniques have their merits. Transducers can be integrated into mould tool walls within a few mm of the processed material, enabling through-transmission to be applied even to closed mould production routes. The pulse-echo technique is totally complementary, extending the application to open processes or production lines where only one-sided access is available. The direct correlation with mechanical properties means the time of flight data can be used as a quantitative guide to the state of cure and eventually to the degree of cure of the final product.

Both dielectrometry and fibre Bragg grating cure shrinkage techniques are hampered by relatively higher costs and complex/time consuming analysis, invariably requiring a greater degree of operator skill and experience for implementation and interpretation. However, both have proved effective enough to track the changes throughout cure from liquid to solid states and beyond into post-cure, providing the most detailed information on cure and material states of the methods listed here.

Despite this, industrial adoption to-date has been limited, possibly due to the seemingly abstract nature of these measurements from the viewpoint of material processors and engineers, combined with the associated uncertainty in their relationship with relevant processing parameters. As a result, users will inevitably require that these methods be correlated empirically with a traditional mechanical/thermal technique for every individual resin system, in order to provide tangible confirmation.

For strain monitoring in particular, the increased adoption of structural health monitoring, where gratings are applied to structures usually for in-service load monitoring applications has increased interest and acceptance of the technology. The evolution of strain as a means of determining cure progress has not been very widely investigated, even though research into processing-induced residual strains has become popular, but this is likely to change as the method becomes more mainstream.

Cure times, generally, may vary simply due to variability or instability associated with the raw material or its environment, composition fluctuations, thermal fluctuations, ambient changes etc which means that assumptions about cure are implicitly made unless monitoring is performed. However, introducing innovative processes is sometimes difficult both technically and also because of the need to overcome the accumulated inertia of long established industrial practices.

There are several types of material, with many different formulations, and a similarly large number of potential processing routes, so it is difficult to be prescriptive about the best technique to use, as no method is universally applicable.

All the techniques described earlier have strengths and weaknesses related to:

- Material sensitivities (small changes or difficult signal)
- Processing applicability (access issues)
- Part integration (internal or external sensor)
- Capital and running costs (sensor durability, re-use and price)
- Volume of material probed (bulk thickness or local, multiple probes).

Cure monitoring has many benefits, principally these can be categorised under two broad areas:

- Quality
- Efficiency.

6.1 Quality

Cure monitoring ensures all components are cured to the required level and exhibit the required performance, whether aesthetic or structural. This results from an increase in component acceptability and a reduction in component variability.

It also encourages improvements and innovation by enabling new materials, designs and processes to be introduced with confidence.

6.2 Efficiency

Implementing cure monitoring means that products are not cured longer than necessary, there is less material wastage and new materials and processes are quicker to establish. This also translates into reduced consumption of services and materials, with temperatures and pressures being applied when necessary and only for as long as necessary.

In summary, the benefits of cure monitoring are:

- Enhanced process control
- Increased productivity
- Increased confidence

- Enhanced quality
- Lower scrap rate
- Saved energy/environment
- Reduced costs!!

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