# TIME-DOMAIN-REFLECTOMETRY CURE MONITORING

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## ABSTRACT

This talk describes a Time-Domain-Reflectometry (TDR) system for monitoring the cure of advanced polymer matrix composites.  A rapid voltage pulse is applied to an inexpensive capacitance sensor, and the returning reflection analyzed quantitatively for viscosity and percent cure.  The returning reflection is either Fourier-transformed to a microwave rotation spectrum for detailed laboratory analysis, or tracked in the direct time domain for robust factory-grade cure monitoring. The advantages of this approach are: 1) an absolute tracking mechanism based on a known polar-group species rather than stray ionic contaminants, 2) a small sensor size due to increased sensor efficiency at microwave frequencies, 3) a microwave measurement technique which is suitably robust for factory application, and 4) the potential use of lines remaining after cure for in-service strain and damage detection.  Results are presented in the Hexcel 8552 and 3501-6 cure systems, both under controlled laboratory conditions and in factory autoclave use. The system provides an alternative between high-frequency fiber-optic methods and low-frequency dielectric methods, combining optical-style precision and miniaturization with electrode simplicity and robustness. The system is important in overcoming quality control problems and improving uniformity in composite manufacture, particularly in critical structures, and in increasing production speed.

KEY WORDS:  Cure Monitoring, Microwave, Sensors

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# 1. INTRODUCTION

**1.1 Background**   Thermoset prepregs used in advanced aerospace composites are highly process sensitive. To assure optimum mechanical properties of laminate end products, cured composites must be void-free, have resin content within a narrow range, and be fully cured. Curing polymeric materials by closed-loop automatic process-control techniques would yield more efficient processes and higher quality high-performance composites products. Sensors that are embedded into the laminates in critical areas, such as in thick areas and joints, that do not adversely affect the quality of the laminate provide more accurate status for active or intelligent cure monitoring and control systems. Additionally, sensors that remain in the cured laminate may be valuable to assess the quality or integrity of the laminate for inspection purposes in production and in the field.

Transducer based sensors follow changes in physical properties by propagating a disturbance wave through the material or tracking the motion of some particle in the material that interacts closely with material structure. The sensing region is well defined and is determined by the transducer placement. A variety of methods are available, including mechanical, acoustical, thermal and electrical; this work focuses on a high-frequency electrical, or more specifically, a microwave dielectric method of sensing.

In-situ sensor methods based on dielectric measurement have been commercialized and are based on the indirect relationship between ion mobility and molecular structure in the thermosetting resin. Typical sensors use interdigital electrode arrays which produce fringing fields with an excitation frequency ranging from DC to 100kHz.[1,2] The selection of the measurement frequency is important in obtaining quantitative data, and higher frequency measurements (> 1 MHz)[3,4,5] are reported to better follow conversion since a dipolar relaxation of the reactant is directly being measured.  The high frequency complex permittivity, which decreases regularly as the reaction proceeds, is affected by the disappearance of specific dipolar species.

**1.2 Dipole Rotation and TDR**   The present paper focuses on a multi-MHz dielectric sensing in commercial aerospace resins to characterize both the viscosity and degree-of-cure during cure. Microwave sensing has the advantage of targeting specific high-frequency rotating polar groups whose chemistry and concentration is well known[6] rather than low-frequency drifting ions resulting from impurities. Rotating dipoles also have intrinsic molecular dynamics independent of sensor configuration[7,8] while conducting ions have no internal dynamics other than charging effects at the electrodes. Rotating dipoles thus provide molecular-level information, which can be used to determine individual cure parameters such as viscosity, percent cure, and degree of sensor contact.  Drifting ions, on the other hand, provide only qualitative indicators of these quantities in a single lumped parameter.

To probe this dipole dynamics, we use an innovative sensing technique that simplifies the measurement considerably.  We use a modified form of Time-Domain-Reflectometry (TDR), where the sensor is measured not with a continuous frequency wave but with a rapid voltage pulse containing a broad range of frequencies at once.[9,10] The reflected signal is captured after an appropriate propagation delay, separating sensor response from connecting-line artifacts on the basis of delay time. The advantage is that the signal can be displayed in either time or frequency domain, allowing the measurement to be adapted to different levels of sophistication.  For R&D the signal is Fourier-transformed to a dipole rotation spectrum, validating results scientifically

and providing a detailed level of analysis. For online process monitoring the direct TDR signal itself is monitored, providing simple output indicators readily integrated with closed-loop control. The same system is used in both cases and scaled-up or scaled-down as appropriate.

# 2. EXPERIMENTAL

**2.1 Background** The specific dipole dynamics follows a standard dielectric relaxation law.[7,8] The dipole's ability to reorient in an electric field, subject to restrictions of the surrounding medium, is given by a frequency-dependent complex permittivity. Real and imaginary components correspond to dielectric storage and loss modulii, similar to mechanical viscoelastic behavior. At low frequencies the dipole follows the applied field such that the storage modulus is high and the loss modulus is low. As the frequency is increased the dipole can no longer follow the field, in which case the storage modulus falls and the loss modulus rises. The characteristic roll-off in storage and peak in loss is called a dielectric relaxation transition, and the frequency at which it occurs is governed by the surrounding viscosity.

Signals are generated and detected by an HP54750 digitizing TDR oscilloscope with a 20 GHz input bandwidth and a 35 ps risetime voltage step. Acquisition is PC-automated, so the scope can be stepped through various time scales with the data transferred to the PC for analysis and storage. A Fisher Scientific programmable lab oven heats the sample through various time/temperature cycles as specified for the material. For factory autoclave testing, a Hyperlabs HL1500 TDR sampler with a 2 GHz bandwidth and 200 ps step provides simple direct-transient monitoring in a robust portable unit.

**2.2 TDR Setup** The basic TDR configuration used to measure this relaxation is shown in Figure 1 . On the left is the TDR signal-source/detector, which applies a rapid (~35ps) voltage step to the line and captures the returning reflection. Extending from the sampling head is a 50-ohm transmission line, which can be several meters long to keep ¼-wave reflections in a convenient position. At the opposite end is the capacitance sensor, consisting of a small air-gap capacitor which radiates a fringing field into the material and detects changes in permittivity.
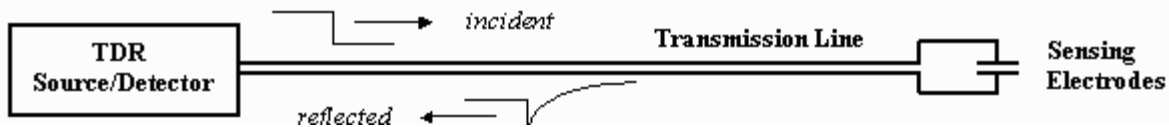


Figure 1 - Basic TDR Sensor Configuration

The complex permittivity of the sample material is found by setting the complex admittance across the sensing electrodes equal to the total current-to-voltage ratio. The total voltage is [$v(\omega)$ + $r(\omega)$], where $v(\omega)$ and $r(\omega)$ are Laplace transforms of the incident and reflected voltages, respectively. The total current is $G[v(\omega) - r(\omega)]$, where G is the characteristic line admittance and the minus sign indicates direction. The total electrode admittance is thus:

$$Y(\omega) = G\frac{v(\omega) - r(\omega)}{v(\omega) + r(\omega)} \qquad (1)$$

with the complex sample permittivity, or storage and loss modulus, given as :

$$\varepsilon(\omega) = \frac{Y(\omega)}{i\omega C_O} \quad (2)$$

where $C_o$ is the geometric capacitance of the unloaded sensor.

Certain refinements are needed to achieve actual results. To remove connecting line distortions and establish a common time reference, Equation 1 is replaced by a network-calibration form, where the reflected signal is calibrated against known reference standards thus removing the input transient from the problem. To resolve rapid signal changes occurring near the beginning of the reflected transient the sampling interval is stepped non-uniformly, thus providing maximum resolution at both short- and long-time extremes. Details of these techniques are found in the references[9,10].

**2.3 Capacitance Sensors**   Electrode sensors are designed to provide appropriate termination impedance to the transmission line over the frequency range of interest.  The reflected signal must be resolvable from both open- and short-circuit baselines over the time interval required for Laplace transform ($1/\omega_2 < t < 1/\omega_1$,  $\omega_1$ and $\omega_2$ are lower and upper frequency limits). In the time domain, this requires adjusting the sensor capacitance to achieve an appropriate decay time. In the frequency domain, it amounts to selecting the capacitance such that the impedance is approximately 50 ohms at the center-frequency of interest.

Electrode sensors can be made in a variety of geometries. A simple coaxial sensor in Figure 2 is made on the tip of 0.9 mm transmission line by cutting back a section of outer casing and Teflon sleeve to leave a protruding inner conductor, and fitting a small machined sleeve over the inner conductor to form a ground conductor. The sleeve diameter is deliberately made undersized to boost the capacitance, and one side of the sleeve is flatted off to expose the inner conductor and allow free flow of resin across the sensing area.  Other coaxial configurations are possible using deposition and chemical-etch methods.
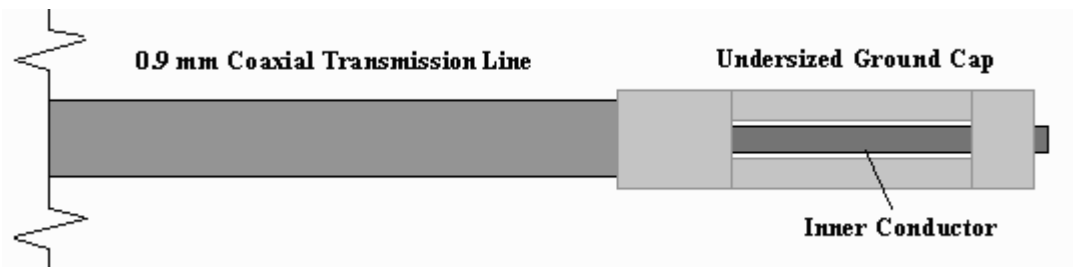


Figure 2 -  Coaxial Capacitance Sensor

**2.4 Planar Capacitance Sensors**   The planar stripline sensor in Figure 3 is our primary sensor configuration due to its low cost and manufacturability.  Both sensor and transmission line are printed on a common substrate using printed-circuit technology.  An entire sheet of sensors is made on a single panel at once and cut into individual ribbon sensors, for a fraction of the cost of individual coaxial sensors.

The sensor and transmission line are patterned on one surface of a 2-sided teflon/copper laminate. The other surface provides a grounded backplane and thus shields the sensor from any metal layup tool on which the sensor rests.  The transmission section is formed in a coplanar waveguide configuration, with a center conducting strip surrounded by two coplanar grounds, thus keeping in a common plane. At the sensor end the center conductor branches into several interlaced

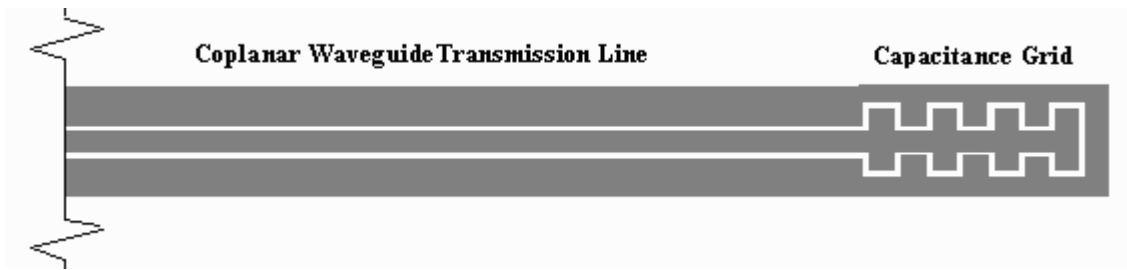fingers, increasing the effective capacitance by increasing the path length with the coplanar ground.



Figure 3 - Planar Capacitance Sensor

Finished sensors have an active sensing area 5 mm wide by 10 mm long, with a transmission path 3 mm wide leading to the sensor. Connection to an external coaxial line is made with an SMA stripline launcher connected to the transmission end of the sensor. After cure the launcher is re-used, so the stripline itself is the only consumable in the measurement. The SMA launcher may be replaced with a mechanical clip-on connector, eliminating any significant cost in the sensor.

# 3. DISCUSION

**3.1 Isothermal Cure**  A typical epoxy dipole relaxation and its variation with cure is shown in Figure 4. The sample is the Hexcel 8552 cure system which contains an epoxy resin and a thermally-activated curing agent. The sample is placed in a glass beaker and heated to 125°C and a 4 pf coaxial sensor inserted as the resin flows. The sensor is calibrated using the bilinear calibration methods[9] with the empty sensor, Chlorobenzene, and Methylene Chloride used as calibration standards.
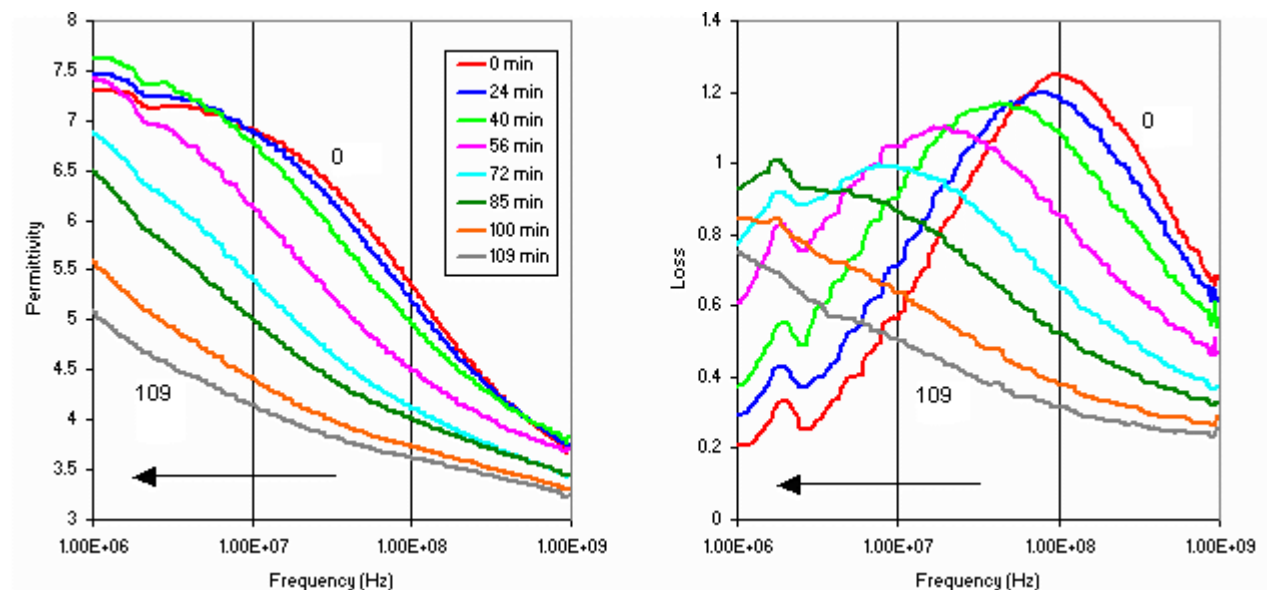


Figure 4 - TDR Complex Permittivity in Hexcel 8552 during 125°C Cure

At 125°C the sample shows a clear dielectric relaxation with the characteristic roll-off in permittivity and peak in loss. The loss peak occurs around 100 MHz, well beyond the range of

low-frequency impedance measurement. The relaxation is dipolar, as evidenced by a semicircular arc appearing in the Cole-Cole complex permittivity plane (Debye Model)[7].

Figure 4 also shows the variation as the sample is held at 125ºC for 2 hours and cured. After remaining stable at 100 MHz for 25 minutes the signal begins to decrease in frequency and amplitude. Over the next 1.5 hours the loss peak drifts continuously downward, from its initial 100 MHz position down to 1 MHz and below, eventually moving below the range of the range of the measurement.

**3.2 Viscosity Relation** Debye[7] derived a simple relationship for the relaxation time of a spherical dipole rotating a Newtonian fluid. The model estimates the time for a polar molecule, originally oriented in an electric field, to relax to its unoriented position under the randomizing action of Brownian motion. The relaxation time is proportional to the volume of the sphere and the viscosity of the medium. The model is satisfactory for dilute solutions of polar materials in non-polar solvents where the dipole shape is approximately spherical. The expression is:

$$\tau = \frac{1}{\omega} = \frac{4\pi a^3 \eta}{kT} = V\frac{3\eta}{kT} \qquad (3)$$

where $\tau$ and $\omega$ are the relaxation time and loss peak frequency, and $a$ and $\eta$ are the molecular diameter and viscosity, respectively.

The cure of a thermosetting resin involves a series of chemo-rheological changes as low molecular weight oligomer is transformed from the liquid to the solid state of a highly cross-linked network. The curing reaction can be monitored by direct measurement of the rheological changes or chemical analysis of the degree of conversion of reactive groups. The change in measured viscosity of the Hexcel 8552 epoxy resin during isothermal cure at 125ºC is used to
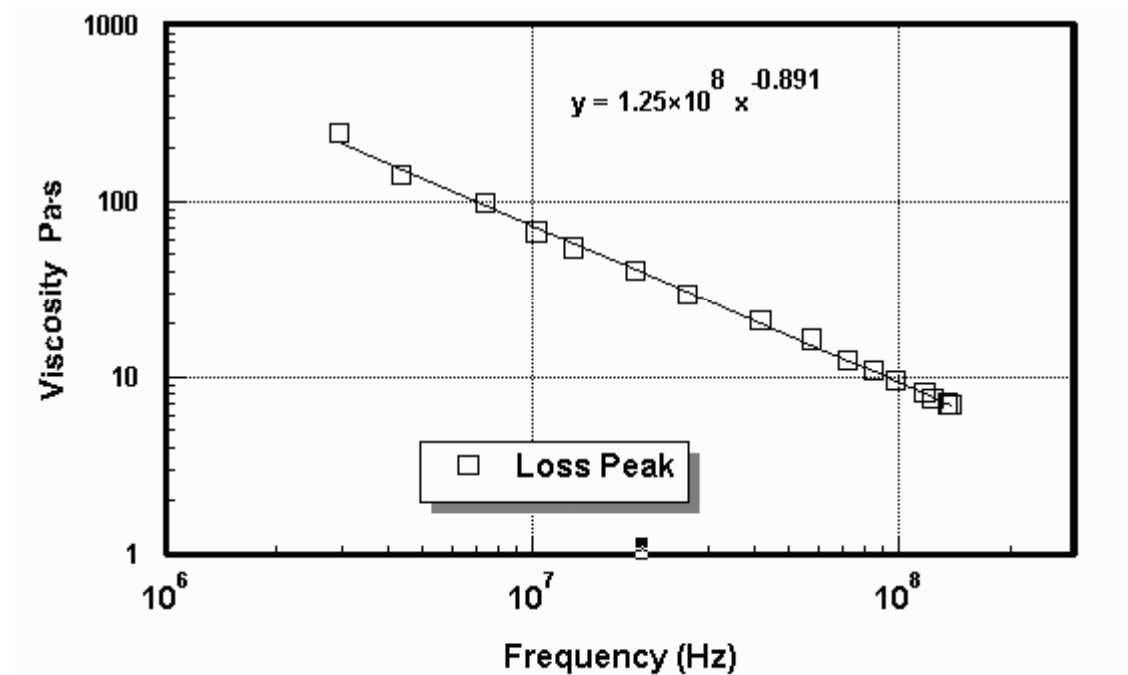


Figure 5 - Loss Peak Frequency vs. Viscosity in Hexcel 8552

calibrate the loss peak frequency - viscosity relation for this particular resin. A Rheometric Scientific RDA instrument was used to determine the viscosity. The TDR loss peak is monitored as a function of time under same cure conditions and is used to produce a plot of loss peak versus viscosity. Power law regression is fitted to the data as shown in Figure 5.

**3.3 Cure Cycle Monitoring**   Next we demonstrate the signal variation during a complete cure cycle, using a time/temperature profile similar to factory autoclave use. The sample is a Hexcel 8552/IM7 graphite-prepreg lay-up in a 5 ply stack and clamped under pressure.  A 0.9mm micromechanical sensor inserted between the plys, with the sensor shielded from the graphite with 2 layers of 8552 glass scrim.  The sample is put though the following cure cycle: 1) ramp to 90°C at 2C°/min, 2) hold at 90°C for 2 hours, 3) ramp to 180°C at 1C°/min, and 4) hold at 180°C for 6 hours.

Figure 6 shows the complex permittivity during the initial ramp to 90°C. The signal moves into the field of view from the left, showing a clear permittivity transition and loss peak as the dwell temperature is approached.  Figure 7 shows the loss peak evolution during the entire cure cycle, in which the peak 1) increases in frequency as the temperature is ramped to 90°C, 2) decreases in frequency slightly as the temperature is held at 90°C and the sample slightly cures, 3) increases in frequency again and falls in amplitude as the temperature is ramped to 180°C and cure begins, and 4) decreases in frequency and amplitude as cure proceeds and the target molecule is consumed in reaction.
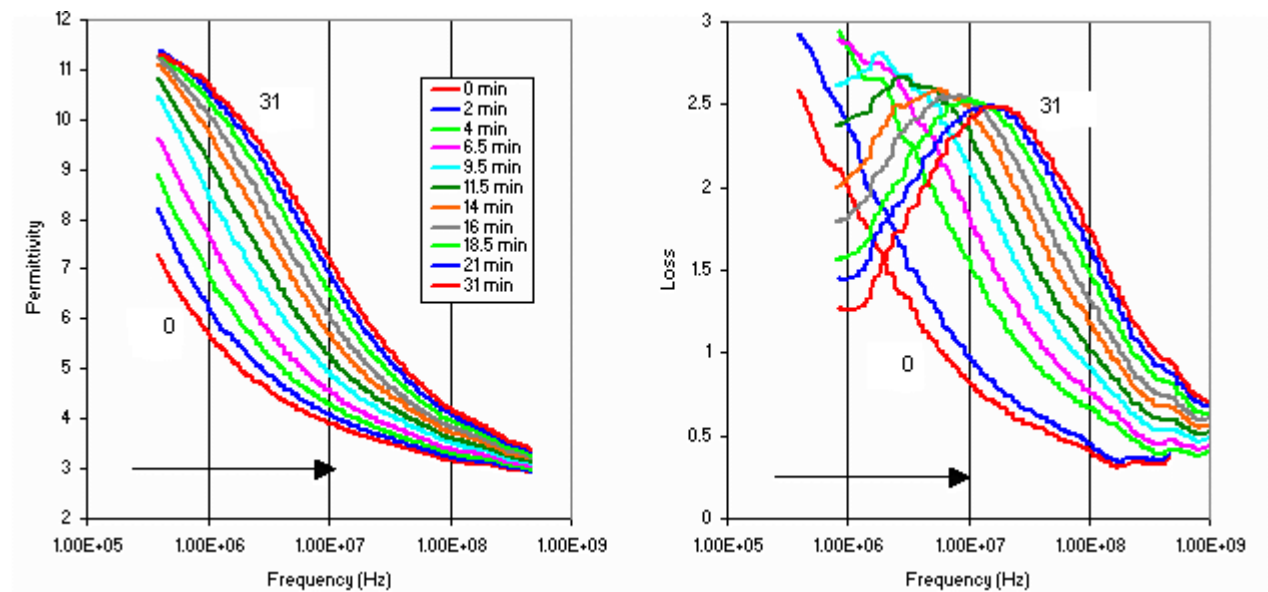


Figure 6 - TDR Complex Permittivity in Hexcel 8552 during 85° C Ramp

Using a polynomial fit we extract the peak frequency from each data file and plot the peak frequency as a function of cure time.  Over half the data files have the loss peak within the field of view, and this range can be extended further if a larger capacitance sensor is used. Using the peak-frequency viscosity relation from Figure 5 we plot the predicted viscosity as a function of cure time, with the result shown in Figure 8.  It is clear that the predicted viscosity follows the same general behavior as the measured rheology data.
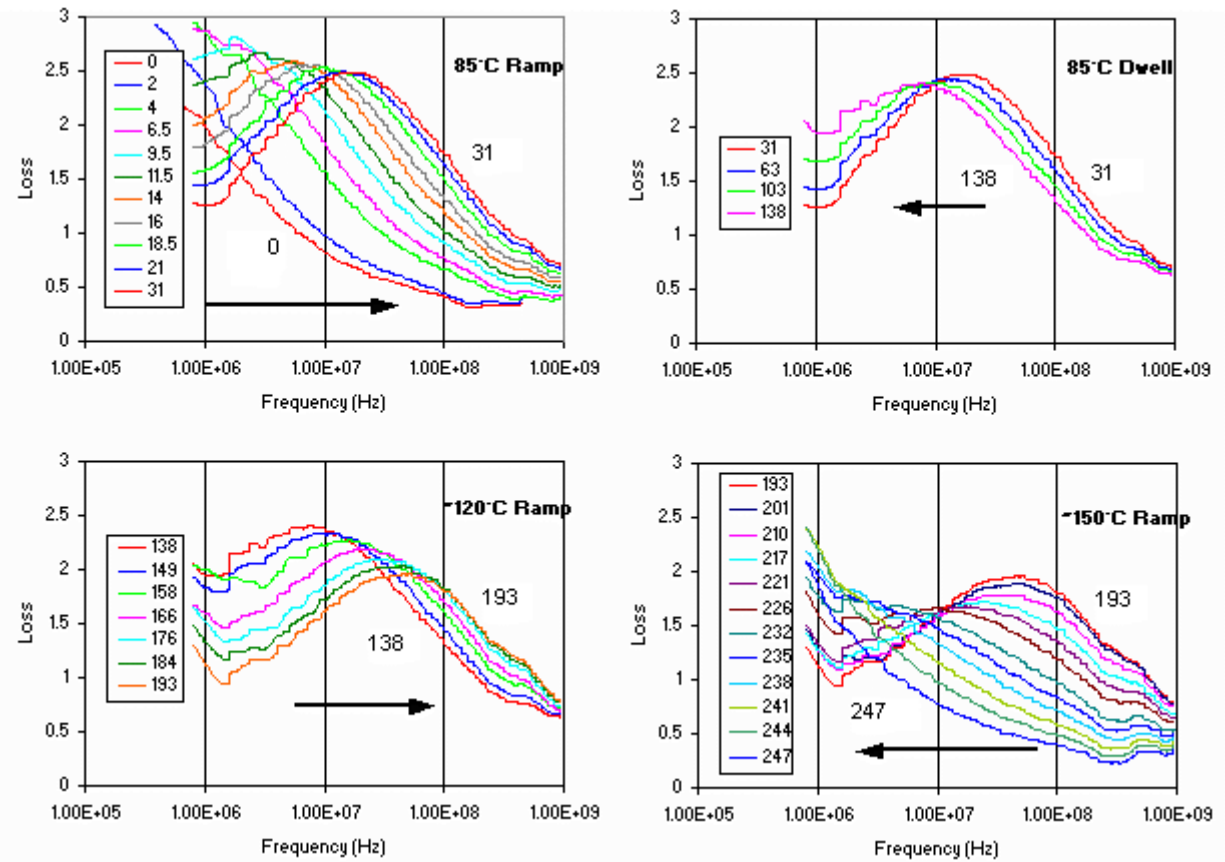
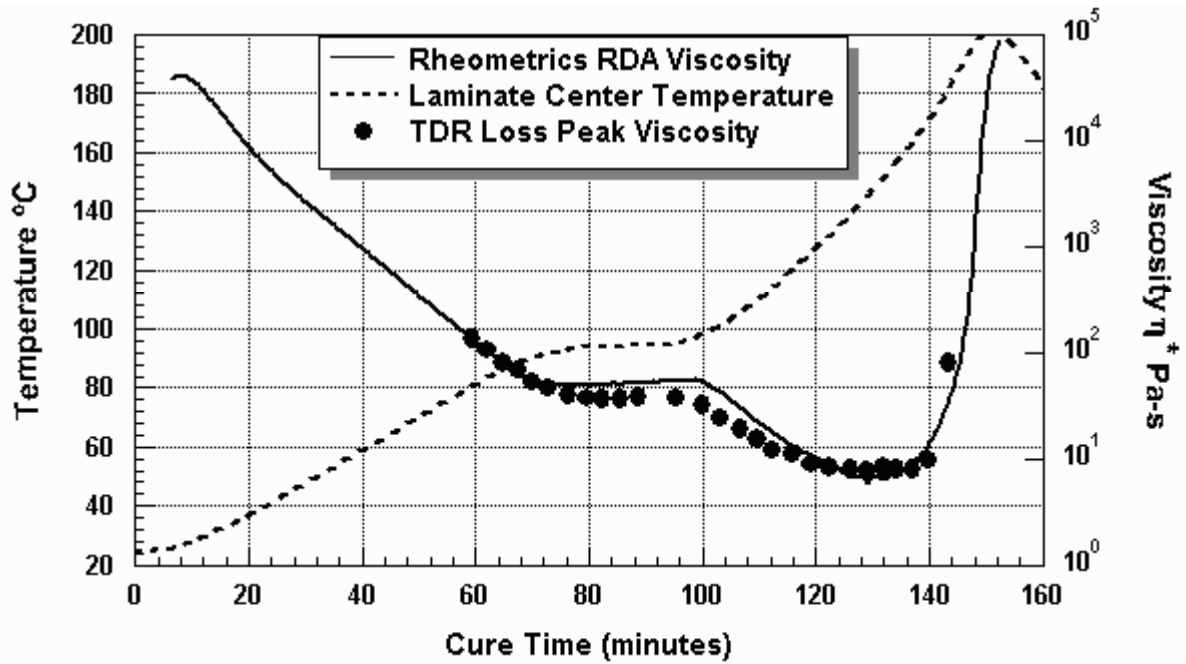Figure 7 - TDR Loss Peak Evolution in Hexcel 8552during Cure Cycle



Figure 8 - TDR Predicted Viscosity vs. Measured Viscosity in Hexcel 8552during Cure Cycle

**3.4 Direct Transient Analysis**  The same features are seen in the direct transient data, from which the frequency data is derived.  From Fourier analysis, high frequency signals in the frequency domain are concentrated at short times in the time domain; low frequency signals in the frequency domain are concentrated at long times in the time domain. A shift in transient amplitude from long to short times in the time domain thus mirrors a shift in transition frequency from low to high frequencies in the frequency domain, and vice-versa.  This forms the basis for direct transient TDR cure monitoring.

The direct transient signal is shown during temperature ramping and cure phases in Figure 9.  In each case the reflected transient is captured on 4 successive time segments, ranging from 100 ps/div on the left to 100 ns/div on the right.  During temperature ramping, the transient amplitude increases on the 100 ps time scale and decreases on the 10 ns time scale. During cure, the transient amplitude decreases on the 100 ps time scale and increases on the 10 ns time scale. The 10 ns increase is smaller during cure, since it is superimposed on an overall amplitude decrease due to the target molecule being consumed in reaction.
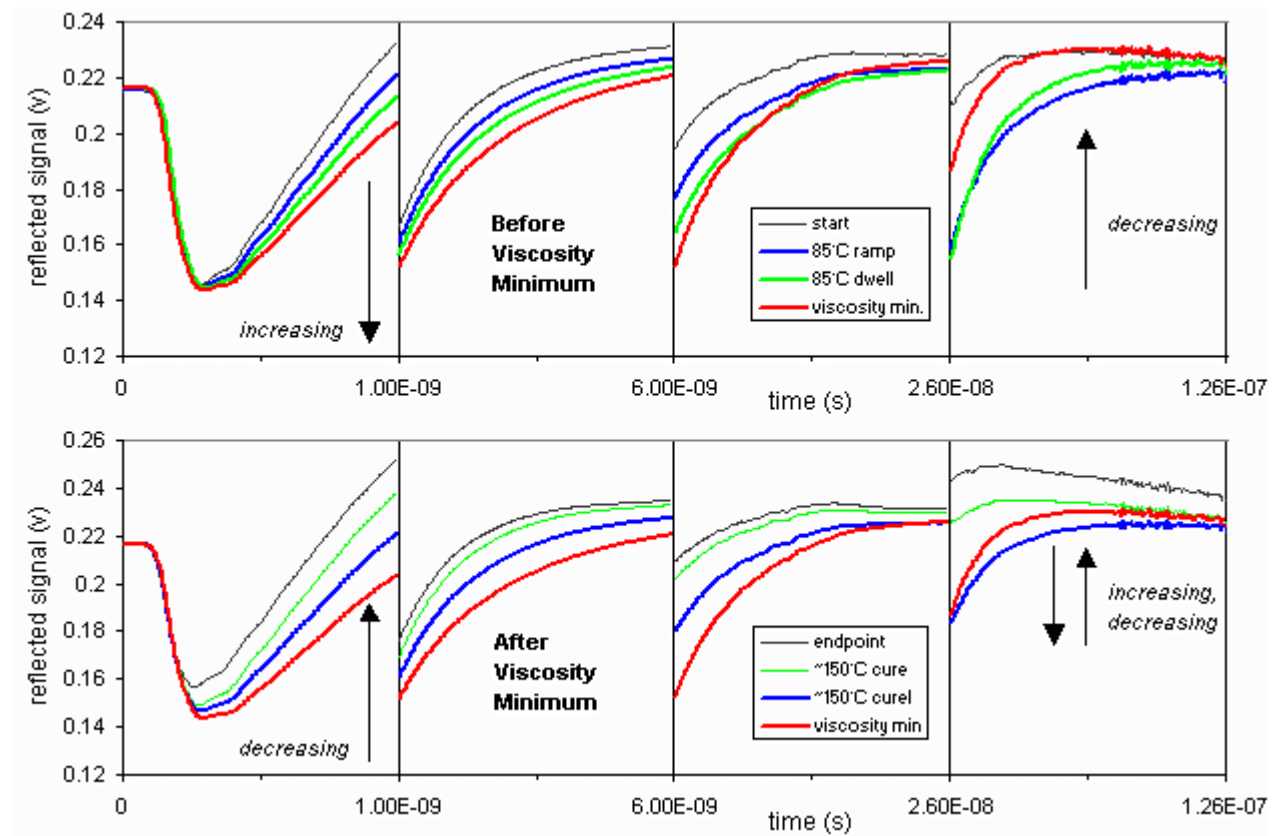


Figure 9 - TDR Direct Transient Signal in Hexcel 8552 during Cure Cycle

When the transient amplitude at 1 ns is plotted as a function of cure time in Figure 10 it qualitatively mirrors the viscosity data. It also tracks during the entire cure cycle, even when the loss peak frequency is below the field of view. The 1 ns amplitude thus provides a "window" on a high-frequency component of the changing dipole spectrum (~1GHz) and rises and falls as the spectrum slides in and out of this window. The measurement provides a simple and robust measurement of high-frequency dynamic response.
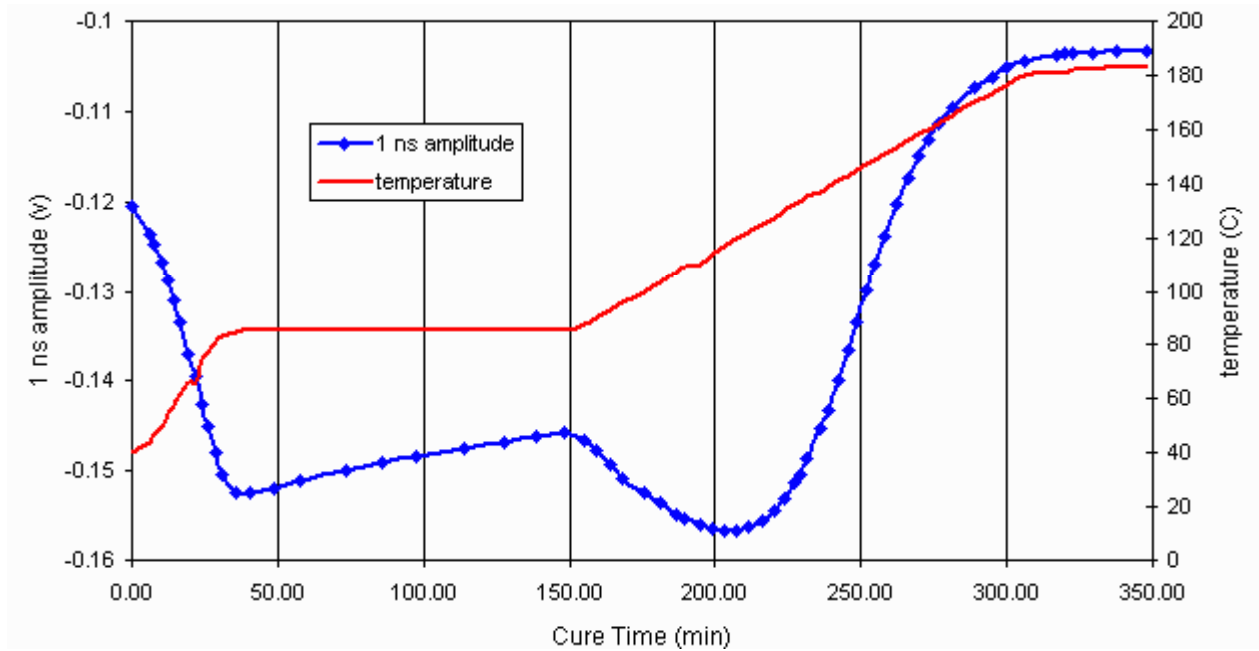
Figure 10 - TDR 1 ns Amplitude Evolution in Hexcel 8552 during Complete Cure Cycle

The transient amplitude at other delays provides additional information. The amplitude at 50 ns in Figure 11 monitors a low frequency component in the changing dipole spectrum (~20 MHz) such that the bulk of the spectrum must pass through this range on its way from low to high frequencies. As it passes through the signal reverses, since the spectrum is now moving away, rather than toward, the field of view. This reversal provides a unique signature, at both the beginning and end of viscosity profile, which can be used to interpret viscosity at points <u>other than the viscosity minimum</u>.
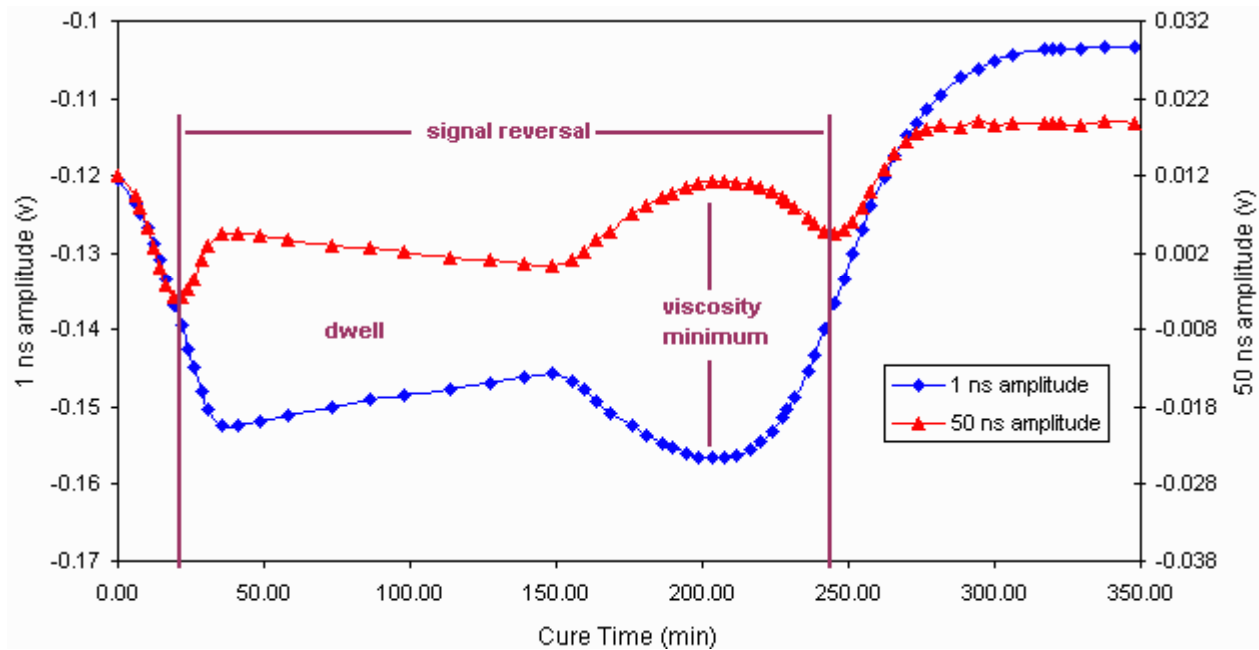


Figure 11 - TDR 1 ns and 50 ns Amplitude Evolution in Hexcel 8552 during Cure Cycle

**3.5 Percent Cure Relation**   Infrared spectroscopy is used in measuring kinetics of the curing reaction and deducing details of the molecular architecture. The FTIR intensity at 906 cm-1 follows the disappearance of the epoxy group during isothermal cure at 125ºC, and thus provides a measure of percent conversion. The area under the 906 cm-1 peak is used to calculate percent conversion, assuming the 100% uncured state is represented by the first measurement.  Isothermal measurements are used since the peak absorption intensities are temperature dependent and therefore lead to complicated analysis for non-isothermal (ramp) conditions.

The direct transient data used to calculate the frequency spectra is compared with FTIR conversion in Figure 12. The transient amplitude at the peak of the reflected signal represents the highest frequency permittivity, and thus provides a simplified indicator of residual dipole groups above the primary viscosity relaxation. The amplitude at 150 ps is plotted against FTIR conversion  with the origin and scaling of the TDR axis chosen to fit the FTIR data.

It is clear that the high-frequency permittivity and corresponding short-time amplitude follow the FTIR conversion data.  Since we are above the range of where the frequency shifts with viscosity, the underlying physical change must be the epoxy dipole concentration[3].
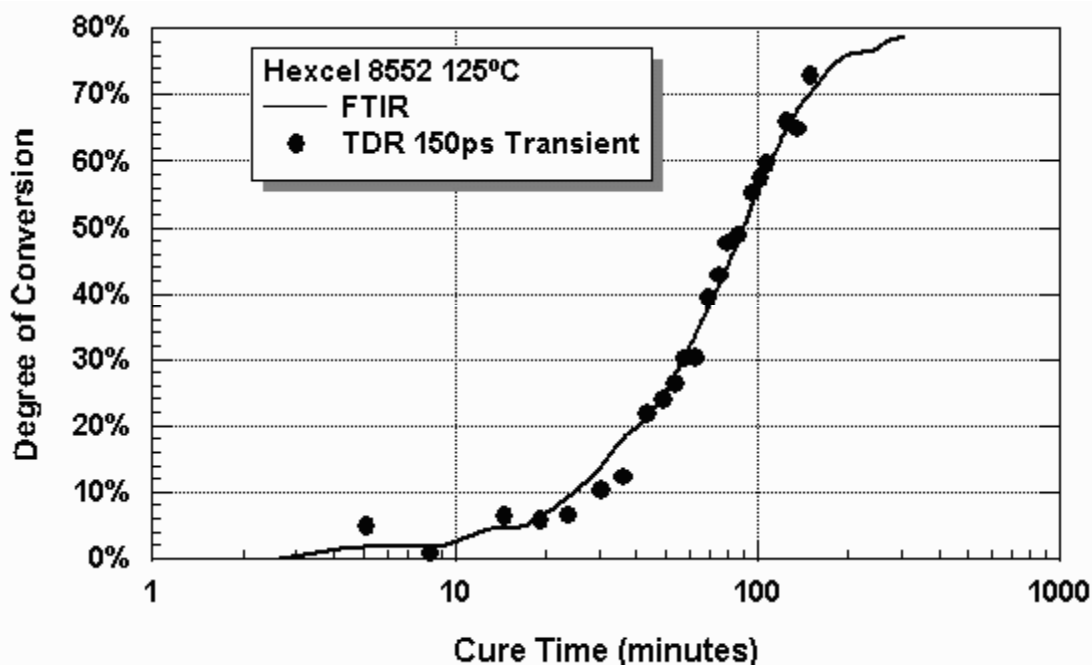


Figure 12 - TDR 150ps Amplitude decrease vs. FTIR

**3.6 Other Cure Systems**   Results can be extended to epoxy based resins other than Hexcel 8552, including 3501-6.  Other cure systems such as PR500 (3M) and RP4005 are also being investigated and will be reported in the future.

# 4. CONCLUSIONS

We have demonstrated at Time-Domain-Reflectometry (TDR) Cure Monitoring System that uses an inexpensive microwave capacitance sensor to monitor resin viscosity quantitatively during cure. The system follows a known polar group with a signature molecular dynamics rather than drifting ions resulting from impurities.

The sensors are small because of the high operating frequency. A picofarad electrode configuration becomes an efficient capacitance sensor operating at TDR frequencies of 100 MHz and above. Further reductions in sensor size may be possible using thin-ribbon planar geometries or submillimeter coaxial geometries with lithography-formed electrodes.

The system can be adapted to different levels of sophistication, either by Fourier-transforming to a dipole rotation spectrum for laboratory analysis or displaying in the direct time for online process monitoring. Analysis of amplitude variations independent of frequency may provide additional information on such parameters as percent conversion and degree of sensor contact.

The system has an additional advantage that the traveling pulse is localized, so the line leading to the sensor can also be used for time-of-flight fault testing when cure is complete. This commonly used form of Time-Domain-Reflectometry could be used for detecting flaws and damage in-service.

# 5. ACKNOWLEDGMENTS

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