

FINAL REPORT
NASA Grant #NAG 1-237**Insitu Frequency Dependent Dielectric
Sensing of Cure**

David E. Kranbuehl
Chemistry and Applied Science
William and Mary
Williamsburg, VA 23187-8795
(757) 221-2542 (Tel) (757)-221-2715 (Fax)

BACKGROUND

With the expanding use of polymeric materials as composite matrices, adhesives coatings and films, the need to develop low cost, automated fabrication process to produce consistently high quality parts is critical. Essential to the development of reliable, automated, intelligent processing is the ability to monitor continuously the changing state of the polymeric resin insitu in the fabrication tool during processing. This sensing capability is essential because 1) resin processing properties vary with age, batch and handling; 2) tool heat transfer properties vary; 3) significant differences exist between one autoclave, press, oven, pultruder and 4) operators differ. In addition, there is the need to quickly develop and optimize cure procedures for new tool designs, new resins etc. This final report discusses the work we did on developing dielectric sensing to monitor polymeric material cure and provides a fundamental understanding of the underlying science for the use of frequency dependent dielectric sensors to monitor the cure process.

Frequency dependent dielectric measurements, often called frequency dependent electromagnetic sensing (FDEMS), made over many decades of frequency, Hz-MHZ, are a sensitive, convenient automated means for characterizing the processing properties of thermosets and thermoplastics.⁽¹⁻²¹⁾ Using a planar wafer thin sensor,

measurements can be made in situ in almost any environment. Through the frequency dependence of the impedance, this sensing technique is able to monitor chemical and physical changes throughout the entire cure process. Dielectric sensing techniques have the advantage that measurements can be made both in the laboratory and in situ in the fabrication tool during manufacture. As such, one application of this work is measurement of the resin's processing properties in situ during fabrication in the manufacturing mold and as input for on-line intelligent closed loop process control.⁽²²⁻³⁰⁾

The FDEMS technique⁽¹⁻²⁾ and related lower frequency work⁽³⁾, can be effective for monitoring a variety of resin cure processing properties such as reaction onset, viscosity, point of maximum flow, degree of cure, buildup in T_g and reaction completion, as well as detecting the variability in processing properties due to resin age and exposure to moisture.⁽³¹⁻⁴¹⁾ The dielectric technique has been shown to be able to monitor similar processing properties in thermoplastics such as T_g , T_m , recrystallization and solvent-moisture outgassing.^(2,42) The technique has the particular advantage over other chemical characterization measurements of being able to monitor these processing properties continuously and in situ as the resin changes from a polymer of varying viscosity to a crosslinked insoluble solid. Another advantage is that measurements can be made simultaneously on multiple samples or at multiple positions in a complex part. Of particular importance is the ability of dielectric sensing to monitor the changing properties of polymeric materials in composites, films, coatings^(43,44) as adhesives in the bondline and to detect phase separation in toughened systems.^(20,21,45-47)

At the heart of dielectric sensing is the ability to monitor the changes in the translational mobility of ions and changes in the rotational mobility of dipoles in the

presence of a force created by an electric field. These variations in molecular position due to an electric field force are a very sensitive means of monitoring changes in macroscopic mechanical properties such as viscosity, modulus, T_g and degree of cure. Mechanical properties reflect the response in displacement on a macroscopic level due to a mechanical force acting on the whole sample. The reason why dielectric sensing is quite sensitive is rooted in the fact that changes on the macroscopic level originate from changes in force displacement relationships on a molecular level. Indeed, it is these molecular changes in force-displacement relationships which dielectric sensing monitors as the resin cures and which are the origin of the resin's macroscopic changes in flow, degree of cure, and other mechanical properties.

One may ask when and why does one need in situ on-line dielectric sensing. There are a number of important reasons and examples. The first major reason is that dielectric sensing allows one to monitor or see the actual state of the material in the tool at all times during the cure process. Temperature and pressure do not provide direct information about the state of the resin. Thus dielectric sensing is one of the few means by which the operator can actually monitor the state of the material during processing and tell what the material is doing throughout the entire fabrication process.

Second, by actually monitoring the state of the material, it is possible to control the fabrication process by data rather than a procedure such as a set time temperature sequence. This means one can have a self correcting automated intelligent cure process which can adapt to variations in material age, fabric permeability, tool heat transfer characteristics, etc.

Third, insitu sensing is needed to verify the veracity and logic of a model's predictions or an operator's reasoning. Making a composite part which passes mechanical tests does not verify that the modeling equations or operator thinking are correct and can be trusted to make predictions.

Fourth, modeling and individual thinking which leads to a procedure driven cure cycle is beset with operating difficulties. Notably, as has been described by George Springer,⁽¹⁴⁾ modeling requires extensive material data characterization of resin properties, as well as fabric and tooling properties which are time consuming to measure and, most importantly, which will vary from day to day and batch to batch. Further, results are limited generally to a particular or a simplified geometry. Fabric preform properties will vary from preform to preform, with lay-up, with bagging and with position within the preform, etc. Heat transfer characteristics will similarly vary with the tool, the autoclave, the position within the autoclave, etc. Thus, given the time and material cost, it is critical to monitor or see what is actually happening and to have the potential to detect, verify, and even correct for these processing property changes as the cure proceeds.

In summary, dielectric sensing provides valuable insight in observing the state of the resin during the process, verifying and reducing the time in developing a cure process, as well as providing an automated self-correcting intelligent control system. Further, dielectric monitoring has, at the same time, the potential to provide on-line quality verification of the fabrication process, thereby increasing product reliability and reducing post-fabrication test costs.

In this report the frequency dependence of the complex permittivity in the Hz-MHZ range is used to separate and determine parameters governing ionic and dipolar

mobility. The quantitative relationship of the ionic and dipolar mobility to monitoring processing parameters such as viscosity and degree of cure during the reaction, is discussed. Several applications of insitu sensing are presented. Finally, the application FDEMS sensing used for closed loop intelligent process control of the cure process is discussed.⁽²²⁻³⁰⁾

Instrumentation

Frequency dependent complex dielectric measurements are made using an Impedance Analyzer controlled by a microcomputer.⁽¹⁵⁾ In the work discussed here, measurements at frequencies from 5 Hz to 5×10^6 Hz are taken continuously throughout the entire cure process at regular intervals and converted to the complex permittivity, $\epsilon^* = \epsilon' - i\epsilon''$. The measurements are made with a geometry independent DekDyne microsensor which has been patented and is now commercially available and a DekDyne automated dielectric measurement system. This system is used with either a Hewlett Packard or a Schlumberger impedance bridge. The system permits multiplexed measurement of 9 sensors. The sensor itself is planar, $1 \times \frac{1}{2}$ inch in area and 5 mm thick. This single sensor-bridge microcomputer assembly is able to make continuous uninterrupted measurements of both ϵ' and ϵ'' over 10 decades in magnitude at all frequencies. The sensor is inert and has been used at temperatures exceeding 400°C and over 1000 psi pressure.

Theory

Frequency dependent measurements of the materials' dielectric impedance as characterized by its equivalent capacitance, C , and conductance, G , are used to calculate the complex permittivity, $\epsilon'' = \epsilon' - i\epsilon''$, where $\omega = 2\pi f$, f is the measurement frequency and C_o is the equivalent air replacement capacitance of the sensor.

$$\begin{aligned}\epsilon'(\omega) &= \frac{C(\omega) \text{ material}}{C_o} \\ \epsilon''(\omega) &= \frac{G(\omega) \text{ material}}{\omega C_o}\end{aligned}\tag{1}$$

This calculation is possible when using the sensor whose geometry is invariant over all measurement conditions. Both the real and the imaginary parts of ϵ^* can have a dipolar and ionic-charge polarization components.

$$\begin{aligned}\epsilon' &= \epsilon'_d + \epsilon'_i \\ \epsilon'' &= \epsilon''_d + \epsilon''_i\end{aligned}\tag{2}$$

Plots of the product of frequency (ω) multiplied by the imaginary component of the complex permittivity $\epsilon''(\omega)$ make it relatively easy to visually determine when the low frequency magnitude of ϵ'' is dominated by the mobility of ions in the resin and when at higher frequencies the rotational mobility of bound charge dominates ϵ'' . Generally, the magnitude of the low frequency overlapping values of $\omega\epsilon''(\omega)$ can be used to measure the change with time of the ionic mobility through the parameter σ where

$$\begin{aligned}\sigma(\text{ohm}^{-1}\text{cm}^{-1}) &= \epsilon_o \omega \epsilon''_i(\omega) \\ \epsilon_o &= 8.854 \times 10^{-14} \text{C}^2 \text{J}^{-1} \text{cm}^{-1}\end{aligned}\tag{3}$$

The changing value of the ionic mobility is a molecular probe which can be used to quantitatively monitor the viscosity of the resin during cure. The dipolar component of the loss at higher frequencies can then be determined by subtracting the ionic component.

$$\epsilon''(\omega)_{\text{dipolar}} = \epsilon''(\omega) - \frac{\sigma}{\omega\epsilon_0} \quad (4)$$

The peaks in ϵ'' dipolar (which are usually close to the peaks in ϵ'') can be used to determine the time or point in the cure process when the "mean" dipolar relaxation time has attained a specific value $\tau = 1/\omega$, where $\omega = 2\pi f$ is the frequency of measurement. The dipolar mobility as measured by the mean relaxation time τ can be used as a molecular probe of the buildup in Tg. The time of occurrence of a given dipolar relaxation time as measured by a peak in a particular high frequency value of $\epsilon''(\omega)$ can be quantitatively related to the attainment of a specific value of the resin's glass transition temperature.

Finally, the tail of the dipolar relaxation peak as monitored by the changing value of $\frac{d\epsilon''}{dt}/\epsilon''$ can be used to monitor in situ during processing the buildup in degree of cure and related end use properties such as modulus, hardness, etc., during the final stages of cure or post cure.

Isothermal Cure

The variation in the magnitude of ϵ'' with frequency and with time for the diglycidylether bisphenol A (DGEBA) amine-cured epoxy held at 121°C is shown in Fig. 1. The magnitude of ϵ'' changes four orders of magnitude during the course of the polymerization reaction. A plot of $\epsilon'' \times$ frequency is a particular informative

representation of the polarization process because as discussed, from eqs. (1-4), overlap of $\epsilon''(\omega) \times \text{frequency}$ for differing frequencies indicates when and at what time translational diffusion of charge is the dominant physical process affecting the loss. Similarly, the peaks in $\omega\epsilon''(\omega)$ for individual frequencies indicate when dipolar rotational diffusion processes are contributing to ϵ'' .

The frequency dependence of the loss ϵ'' is used to find σ by determining from a computer analysis or a log-log plot of ϵ'' vs. frequency, the frequency region where $\epsilon'' \times \text{frequency}$ is a constant. In this frequency region the value of σ is determined from eq. (3).

Figure 2 is a plot of $\log(\sigma)$ vs. $\log(\text{viscosity})$ constructed from dielectric data and measurements on a dynamic rheometer. The figure shows that at a viscosity less than 1 Pa s, (10 P), σ is proportioned to $1/\eta$ since the slope of $\log(\sigma)$ vs. $\log(\eta)$ is approximately -1. The gel point of the polymerization reaction occurs at 90 min based on the crossover of G' and G'' measured at 40 rad/s. This is very close to the time at which η achieves 100 Pa s, which is also often associated with gel. The region of gel marks the onset of a much more rapid change in viscosity than with σ . This is undoubtedly due to the fact that as gel occurs the viscoelastic properties of the resin involve the cooperative motion of many chains while the translational diffusion of the ions continues to involve motions over much smaller molecular dimensions.

Figure 3 is a plot of $\log(\sigma)$ vs. degree of cure determined from differential scanning calorimeter measurements. The approximate exponential dependence of σ on α is not surprising since α is approximately exponentially related to viscosity through $\eta = \eta_0 \exp(E/RT + K\alpha)$. Again there is a break in the dependence of σ on α as the value of σ drops from 10^{-9} to $10^{-10} \Omega^{-1} \text{ cm}^{-1}$ in the region of gel.

The time of occurrence of a “characteristic” dipolar relaxation time can be determined by noting the time at which $\epsilon''_{\text{dipolar}}$ achieves a maximum for each of the frequencies measured where $\tau = 1/2\pi f$ at the time at which $\epsilon''_{\text{dipolar}}$ achieves a maximum for the frequency, f . Values of τ can be measured over a range of frequencies and temperatures.

Figure 4 reports values of $\log(\tau)$ vs. $1/T$ at incremental changes in the degree of advancement α . Like $\log(\sigma)$, the values of $\log(1/\tau)$ are related to the viscosity and the extent of cure as is observed on Figs. 2 and 3. Because the values of τ occur in the post-gel, pre-glass region of cure, 90-300 min, these values of τ are appropriately analyzed as an α -relaxation associated with the T_g to $T_g + 100^\circ$ region.

A Vogel-Fulcher-Tammann-Hesse equation can be used to characterize the temperature dependence of the relaxation times for these six different degrees of cure, 0.70, 0.75, 0.80, 0.825, 0.90 and 0.95:

$$\log \tau = A + \frac{B}{T - T_\infty}$$

The best fit occurs at T_∞ values 50°C below the respective values of T_g for each of these values of α . T_g was determined by advancing the reaction to a particular value of α based on the time-temperature DSC kinetic data. The softening temperature, T_g , was determined from the onset of the drop in G' .

Figure 5 is a plot of $1/(T - T_\infty)$ vs. τ , where $T_\infty(\alpha) = T_g(\alpha) - 50^\circ\text{C}$. The observation that the value of τ changes with T_∞ suggests that the parameters A and B show little variation in this pre-glass region. Further the results show that the time of occurrence of successive increases in the relaxation time monitors the value $(T_{\text{rx temp}} - T_g)$. Thus

through the Fulcher equation, the ϵ'' relaxation peaks can be used to measure the build-up in T_g and degree of cure as the polymerization proceeds.

Monitoring Cure in Multiple Time Temperature Processing Cycles

As a representative example of cure monitoring using a common commercially used aerospace resin and a complex cure cycle, Figure 6 displays the output of $\omega \epsilon''(\omega)$ for a two stage, 121°C and 177°C, ramp-hold sequence used to cure a commercial widely used MY720 aromatic epoxy system. This resin consists of a tetraglycidyl 4,4' diamino diphenylmethane (TGDDM) and diamino diphenyl sulfone (DDS). This system with catalyst is sold by the Hercules Corporation as 3501-6.

Figure 6 shows two peaks of the overlapping $\omega \epsilon''(\omega)$ lines. These indicate the times and magnitude of maximum flow as monitored by the ionic mobility. The first peak, the highest degree of flow, occurs at the beginning of the first hold. The second point of high flow, high ionic mobility, occurs midway up the ramp between the 121° hold and the 177° hold. As the temperatures rises the fluidity increases until such time as the rate of reaction and thereby the degree of cure which is also increasing during the temperature ramp overwhelms the temperature effort on fluidity. At this point the fluidity begins to drop and a peak in $\omega \epsilon''(\omega)$ occurs indicating the second occurrence of maximum flow.

The gradual drop in the magnitude of $\epsilon''(\omega)$ during the final hold and its rate of change $\frac{d\epsilon''}{dt}$ monitor the buildup in modulus and its rate of buildup. When ϵ'' attains a constant value, the system has reached its final lowest value of dipolar ionic mobility. Thus when no further changes in mobility can be detected, $\frac{d\epsilon''}{dt} = 0$, the system is fully reacted at that hold temperature. Monitored in this way, the changing values of ϵ'' are a very sensitive means of detecting the final small changes in degree of cure and

the buildup in end use properties such as Tg, modulus, etc. Figure 6 suggests even after a 2 hour hold, for this fresh 3501-6 resin the mobility is still decreasing and final cure or end use properties have not been attained.

Figure 7 shows the correlation between the viscosity and the ionic mobility based on isothermal runs for this system as monitored by the value of ϵ'' (5 kHz). A representative calibration curve relating the FDEMS sensor output to degree of cure is shown in figure 8. Unlike viscosity, separate calibration curves for different temperatures must be generated from the isothermal runs because they are temperature dependent.

The buildup in final cure properties such as degree of cure during the last hold is monitored with a high degree of sensitivity using the value of $\frac{d\epsilon''}{dt}/\epsilon''$. Figure 9 is a correlation plot of the normalized rate of change in ϵ'' (5 kHz) compared with model predicted values (based on numerous DSC runs) of the buildup in the degree of cure.

Figures 10 and 11 show two important applications of FDEMS sensing as applied to processing of an epoxy system. Figure 10 shows the effect on processing properties as monitored by the value of $\omega\epsilon''(\omega)$ for this system when the first hold temperature drifts 10° higher, 131°C. Figure 11 shows the output for the original 121°, 177° ramp hold sequence but for a batch of 3501-6 epoxy resin after it has been left to age at room temperature for 30 days.

Even without the calibration relations the effect on cure processing properties can be clearly seen from the sensor output. In Figure 10, the value of ϵ'' peaks a little higher but drops much more rapidly. The second peak in ϵ'' during the ramp is much lower. Thus the effect of the 131° hold is to cause a slightly higher fluidity initially.

But the high fluidity region lasts for a much shorter time. Equally important at the second point of high fluidity, which is usually critical for composite-prepreg consolidation, the fluidity is significantly lower. The overall effect of aging is seen as decreasing the level of fluidity through out the cure procedure. Full cure is achieved much sooner in the final hold for the aged resin as the value of $\frac{d\epsilon''}{dt}$ approaches zero

much sooner.

Monitoring Cure in a Thick Laminate

A major advantage of the FDEMS sensing technique is the capability of monitoring and quantitatively measuring processing properties in situ during cure in complex shaped parts during processing in autoclaves, presses and pultruders.

For example, sensors can be placed in a thick 192 ply Hercules 3501-6 epoxy-graphite laminate at multiple positions (see Figure 12) such as the tool surface, at 32 plies, at 64 plies, and in the center at the 96th ply. This 192-ply composite layup with the embedded sensors was cured in an autoclave. The output at each sensor was measured automatically at intervals throughout the cure cycle by multiplexing the four sensors through a computer-controlled switch to the impedance bridge. The multiplexed sensor-bridge-computer system can make more than 100 permittivity measurements in less than 2 minutes. Measurements are recorded continuously throughout the cure cycle without interruption over the 10^6 - 10^{-2} range in magnitude of ϵ' and ϵ'' .

Figure 13 is a plot of the viscosity determined by the sensor at each of the four positions in the thick laminate during cure in the autoclave. The FDEMS sensor data

show that the middle ply achieves its first viscosity minimum 20 minutes after the plies on the surface of the tool plate. The middle plies continue to lag the surface ply until the second ramp to 177°C. At this point the exothermic 3501-6 epoxy reaction starts heating the laminate from the inside. As a result, the heat generated at the center ply causes the viscosity to catch up with the viscosity of the surface plies. In this way, FDEMS sensor output measurements of the viscosity at the center and surface can be used to evaluate the cure cycle. In this example the center and surface plies achieve their viscosity minimum in the high temperature ramp at roughly the same time. At all earlier times the center lags the reaction at the surface.

Thus the sensor not only reveals what is occurring during cure throughout the part but it also reveals the exact time-temperature-magnitude dependence of processing properties such as viscosity for that tool, geometry and particular run.

The sensor output can be used to test the validity of processing models such as the Loos-Springer model.⁽¹¹⁾ Sensor measured values of η can be compared with the Loos-Springer model predictions. Figure 14 is a comparison of the model's predictions and the measured values at the 64th ply. Agreement in the viscosity's time dependence and magnitude with the predictions of models is essential if the model is to be verified and used with confidence.

The sensor output can also provide useful input for controlling the cure cycle. For this epoxy the most widely recommended and successful cure cycle forces the second viscosity minima to occur at the same time throughout the laminate's thickness as seen from the results of Figure 13. Thus one can hypothesize that an efficient and effective cure cycle causes the viscosity minima at the surface and center to occur at the same time, and as rapidly as possible. Accordingly, one might propose raising

rapidly the air temperature in the FDEMS sensor-controlled run until the exotherm at the center causes the viscosity at the center ply to start to catch up to the surface viscosity. At this point the air temperature could be rapidly lowered, to hold the surface viscosity in this high flow condition while the center viscosity catches up. At such point as the center viscosity goes through its viscosity minimum and advances beyond the surface plies, the air temperature would be set to the final 177°C hold. The 177°C hold would continue until the sensor output indicated, through $\frac{d\epsilon''}{dt}$ approaching zero, that the reaction was complete.

Figure 15 shows the results from such a sensor controlled run in an autoclave at NASA. FDEMS sensor-measured viscosities from two sensors at the center ply and one sensor at the surface ply are shown in Figure 15. Air autoclave temperatures and the temperatures at the surface and center ply are also shown. The starting time for the FDEMS sensor-controlled autoclave run and the manufacturer's cure cycle run are defined as the time at which the tool surface temperature starts to increase.

The FDEMS sensor-controlled run significantly reduced the time lag and viscosity difference between the center ply and the tool surface ply. The amount of flow as measured by the magnitude of the viscosity minimum was greater in the FDEMS sensor-controlled run. The approach of $\frac{d\epsilon''}{dt}$ to zero was used to determine cure completion. The total cure time of 200 minutes in this FDEMS controlled run is 40 minutes less than the conventional cure cycle.

Resin Film Infusion

As an example of cure monitoring in resin film infusion, Figure 16 shows the output of $\omega\epsilon''(\omega)$ from sensor 1 for the MY720 aromatic TGMDA epoxy system commercially sold as 3501-6 by Hercules.

Measurements were taken of ϵ'' at 3 minute time intervals during an RFI, resin film infusion cure cycle in an autoclave at the Northrup Corporation Los Angeles plant. The T stiffened graphite preform shown in Figure 17 was furnished by the Douglas Aircraft Company. Temperature holds occurred at approximately 120°C and 177°C. Three frequencies 250, 500 and 500 Hz are shown in Figure 17. The time the resin front infiltrates to the sensor's location is shown by the large jump in sensor output. The overlapping lines indicate the signal is dominated by ionic mobility until the second hold has been reached. Figure 7 shows the correlation between the viscosity and the ionic mobility dominated values of ϵ'' at 5.0 kHz. Figure 7 was generated with data taken at temperatures between 100 and 149°C. It shows $\epsilon''_{\text{ionic}} \propto 1/\eta$ for viscosities up to 10^3 poise, at which point the relation between the "molecular viscosity" governing ionic mobility no longer is directly related to the reciprocal of the macroscopic viscosity as measured on a dynamic mechanical viscometer. As discussed, this approximate inverse relation between molecular mobility and viscosity breaks down as the resin begins to crosslink and gel. Thus, FDEMS sensing can be used to quantitatively monitor viscosity insitu during processing. Through correlation with other techniques, FDEMS can be calibrated to detect gel. A calibration curve relating degree of cure and the FDEMS sensor output has also been generated, Figure 8. Unlike the viscosity calibration curve, it is temperature dependent. The buildup in final cure

properties such as degree of cure during the last hold was monitored insitu using the FDEMS $\frac{d\epsilon''}{dt}/\epsilon''$ output and the correlation plot shown in Figure 9 for 3501-6.

Figures 18 and 19 show the viscosity and degree of cure of two different positions on the preform, position 1 on the flat panel and position 3 at the top of the T stiffener (see Fig. 17) these results are obtained from the FDEMS sensor output as shown in Figure 16 and using the calibration plots such as shown in Figure 7. Wetout times at the nine sensor locations shown in Figure 7 are:

Sensor Location	1	2	3	4	5	6	7	8	9
Wetout Time (min)		63	104	168	114	97	168	110	1 0 0
									163

Smart Automated Control

A smart artificial intelligence control system is based on monitoring the actual *state* of the resin, not on a predetermined time temperature procedure. Thus the temperature scheme the part experiences is not based on time, but on the achievement of molecular landmarks in the curing process. Because these critical points may not occur at the exact same time for each part being made, time is not wasted holding a part at some stage when the cure process could be advanced. This gives the smart, closed-loop process a flexibility to adjust to variations in resin cure and heat transfer properties. Thus it is much more efficient and reliable than a rigid time temperature procedure.

An intelligent closed-loop system produces more consistent parts. The resin's advancement to the next stage of cure is based on its achieving a certain molecular

state. Consequently, with each part made, wet-out of the fibers is defined by monitoring the position of the resin front. The advancement of the viscosity and degree of cure is monitored. Final cure is defined by a universal degree of cure. This is a more consistent way to produce high composite parts than simply subjecting them to the same time/temperature schedule when batch variations and differences in prefabrication handling are present.

A smart closed-loop system is composed of a heating/pressure device, such as a press or autoclave, sensors able to gather data insitu from the composite part, and smart software that collects the sensor information, interprets it, and then makes decisions that control the fabrication device. The smart software combines both the predictions of the processing model and the insight of operator experience. Figure 20 is a schematic of the FDEMS sensor smart system for insitu monitoring of cure and for expert automated process control. The expert system was constructed to optimize and control the achievement of six critical stages during the resin film infusion cure process. These were: 1) achieve a low resin viscosity; 2) maintain a low viscosity until impregnation is complete, 3) advance the resin reaction at an intermediate temperature to a particular degree of cure that avoids an excessive exothermic effect (this value varies with part thickness), 4) ramp to final cure temperature once reaction has advanced, 5) monitor degree of cure during final hold, 6) determine achievement of proper degree of cure, which is related to attainment of ultimate T_g , and desired use properties and then 7) turn the process cycle off.

Figure 21 shows the sensor output for the smart automated sensor expert system-controlled run. The resin reached the center sensor at 37 min. The viscosity is maintained at a low value by permitting slow increases in the temperature. At 60

min. The fabric impregnation was complete. The resin was advanced during a 121°C hold to a predetermined value of degree of cure $\alpha = 0.35$, based on the model's predictions of the extent of the exothermic effect. This value of α is clearly dependent on panel thickness. At this point, 130 min. The ramp to 177°C was begun. Achievement of an acceptable complete degree of cure was determined by the sensor at 190 min. Then the cure process was shut down.

As an aside, we note that the FDEMS sensor input information can also be used to detect the onset of phase separation in toughened thermoset systems and to monitor cure in thin film coatings and adhesive bond lines. Particularly important, the FDEMS sensor is also very sensitive to changes in the mechanical properties of the resin due to degradation. As such, it can be used for accelerated aging studies and as a dosimeter to monitoring the composite part during use to determine the knockdown in the required performance properties with time.

In summary a FDEMS sensor system can be used to monitor the processing properties insitu during the fabrication process of a composite part.

A "smart" sensor control system can be used to monitor resin properties for reproducibility-quality assurance, to ensure fabric impregnation, and to intelligently control and optimize through insitu sensor feedback the composite fabrication process.

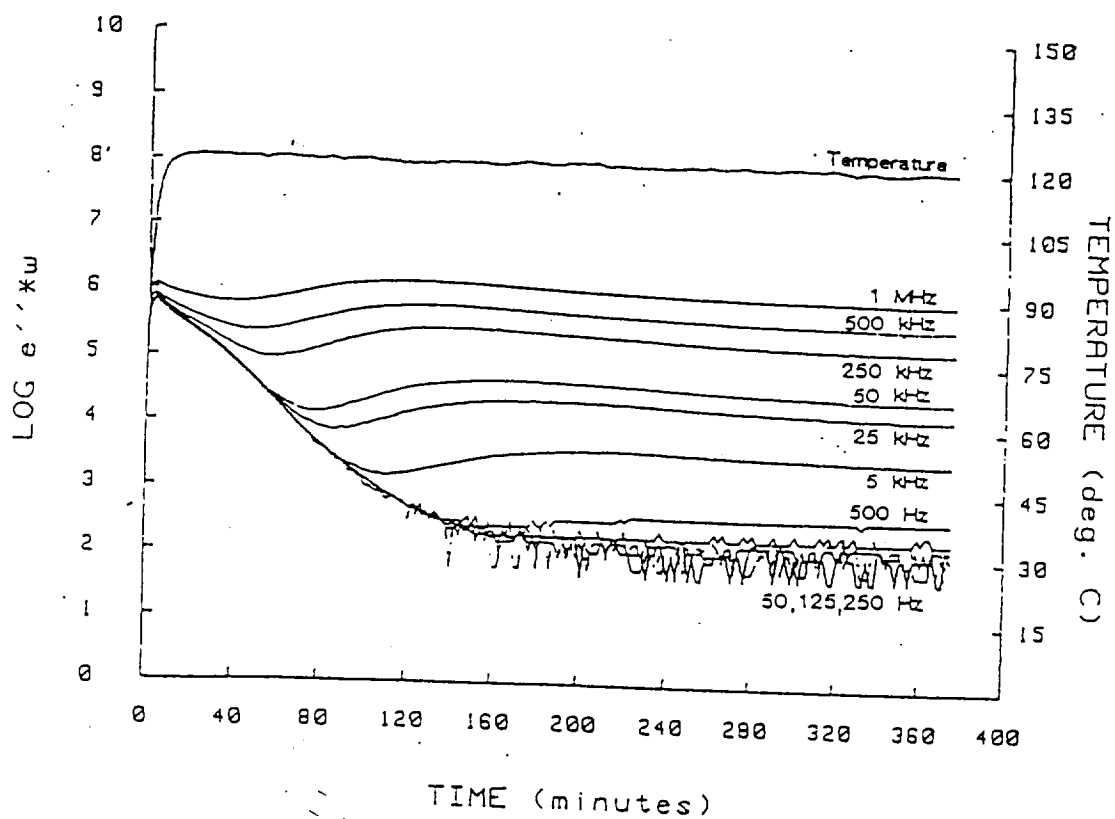


Figure 1 $\text{Log } \epsilon'' \omega$. Versus time during a 121° isothermal polymerization.

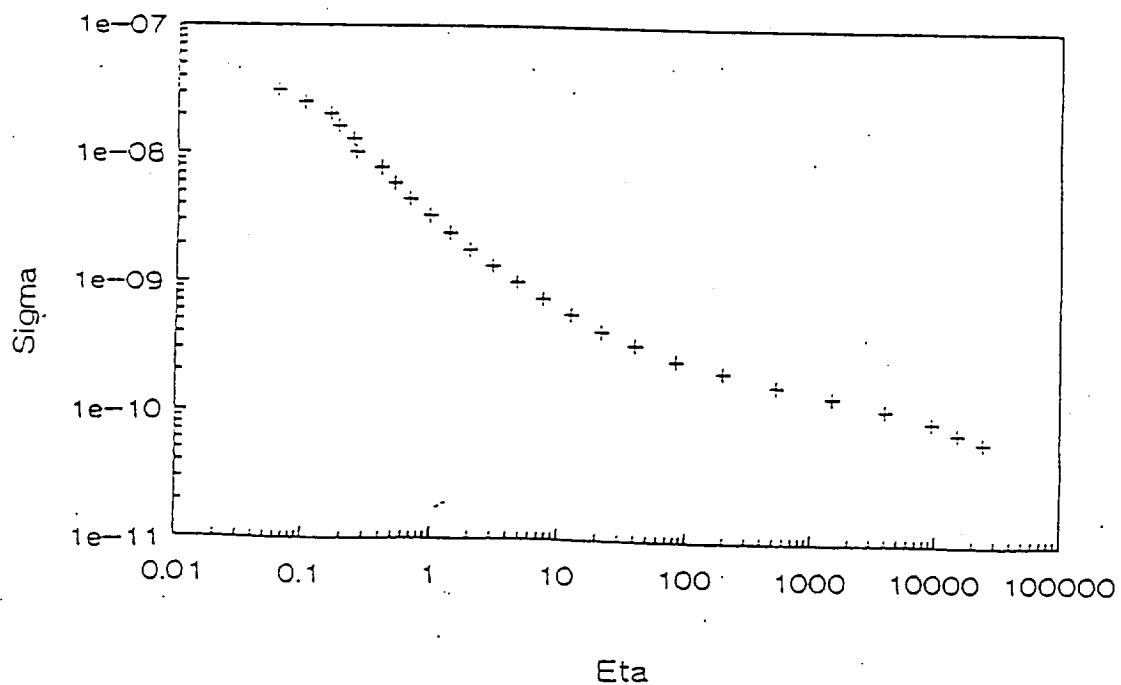


Figure 2 $\text{Log } (\sigma)$ versus log (viscosity) during a 121° polymerization.

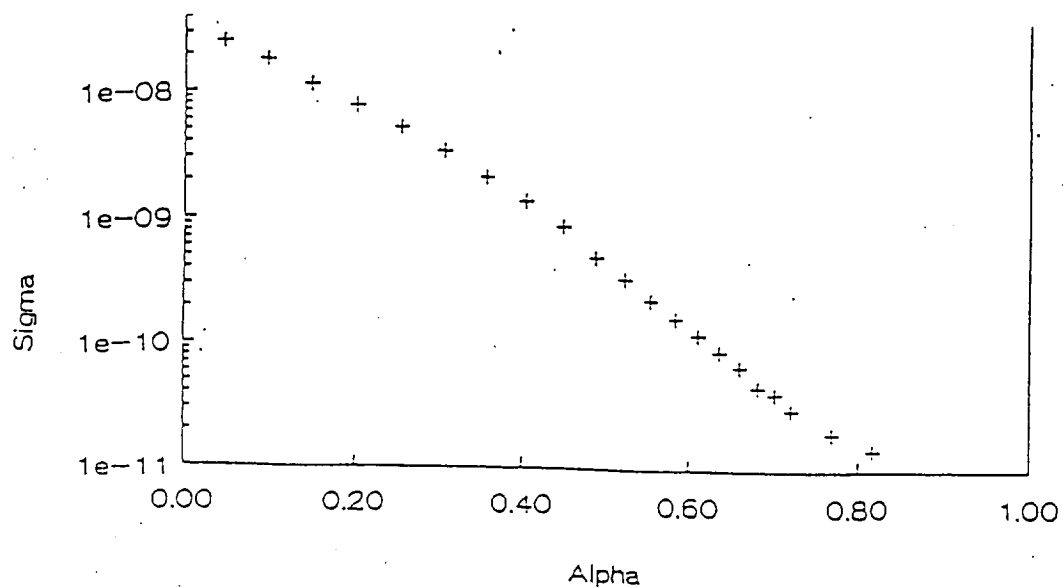


Figure 3 Log σ versus degree of cure α during 121° isothermal cure.

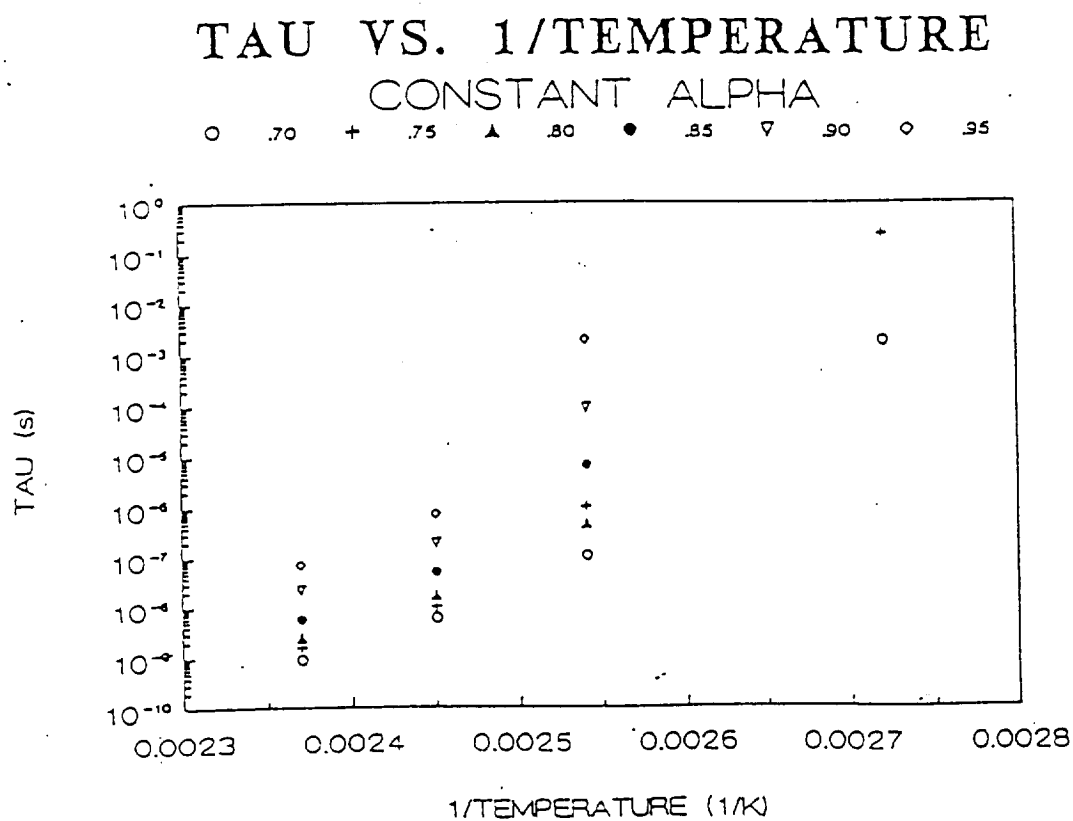


Figure 4 Log (τ) versus $1/T(^{\circ}\text{K})$ at comparable degrees of advancement between .70 and .95.

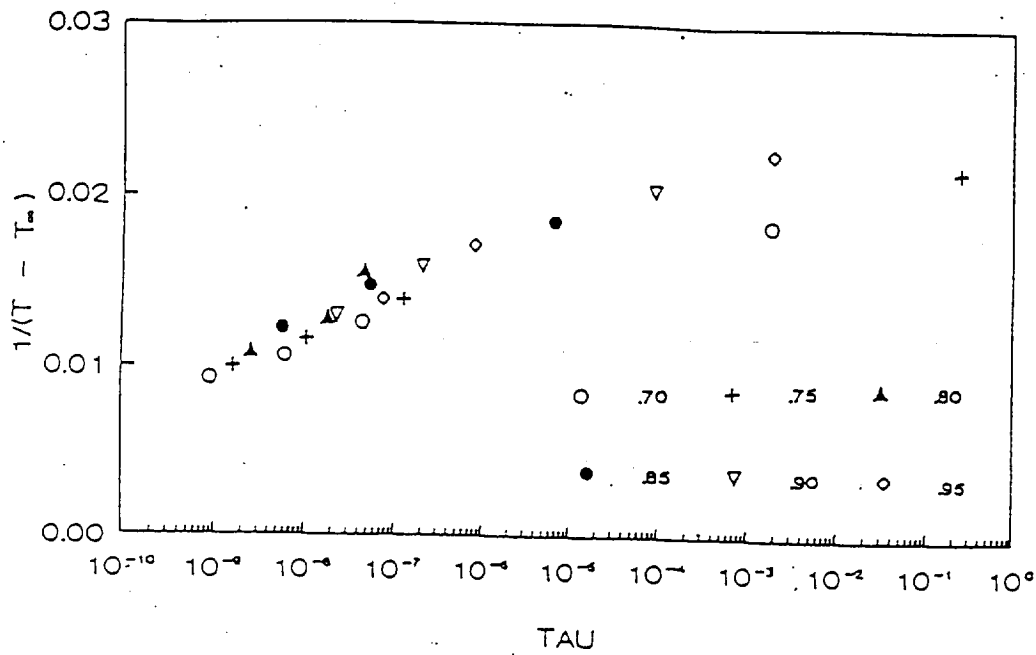


Figure 5 $\log(\tau)$ versus $1/(T - T_{\infty})$ where $T_{\infty} - T_g(\alpha) - 50^{\circ}$

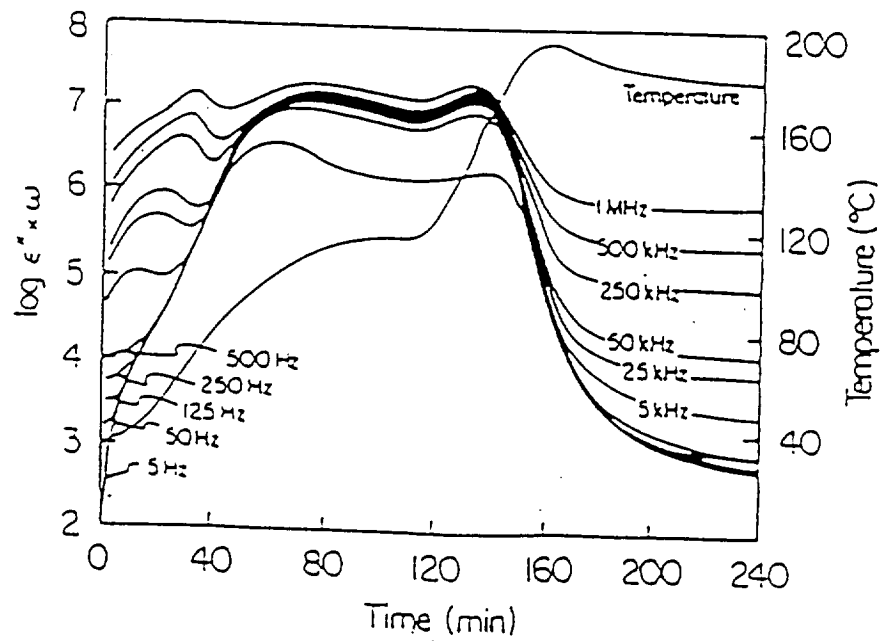


Figure 6 Plot of $\epsilon'' \times \omega$ versus time of the sensor output at the 64th ply of the thick

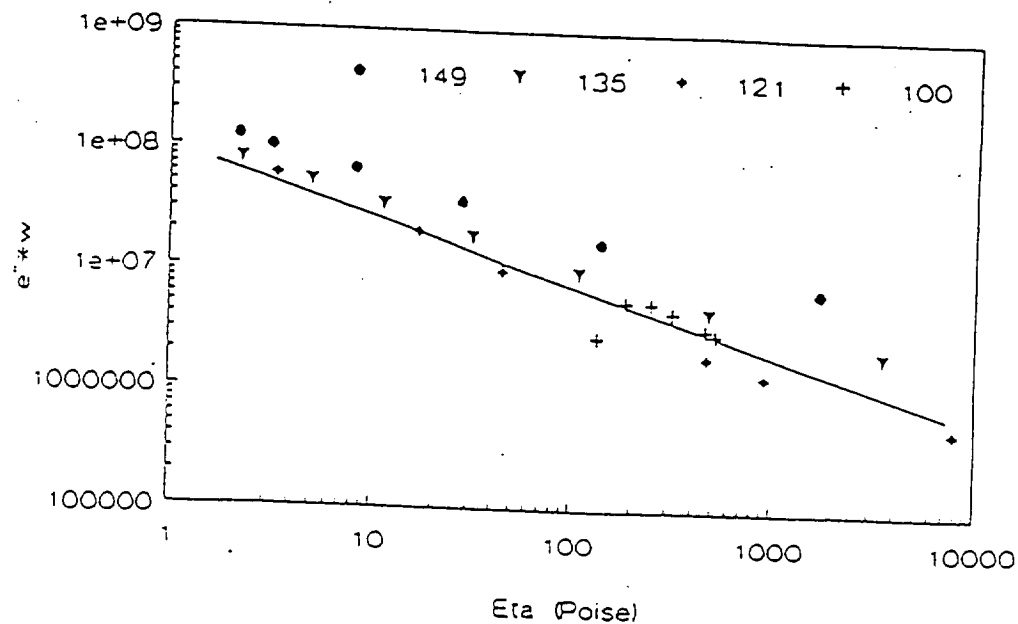


Figure 7. $\text{Log } \omega \epsilon''(\omega)$ versus log (viscosity) for the TGDDM epoxy based on 4 iso thermal runs.

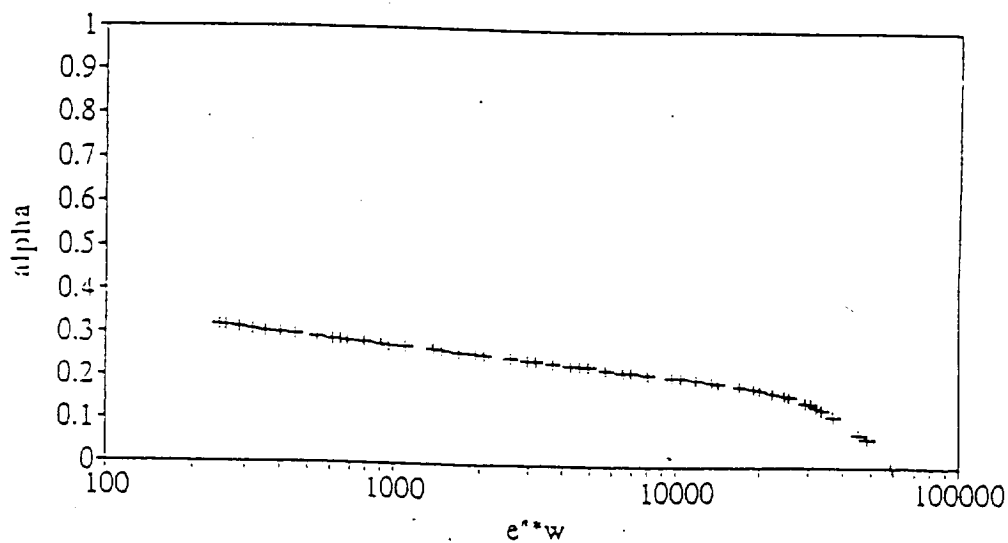


Figure 8. Correlation curve relating degree of cure to $\omega \epsilon''(\omega)$ at 135°C.

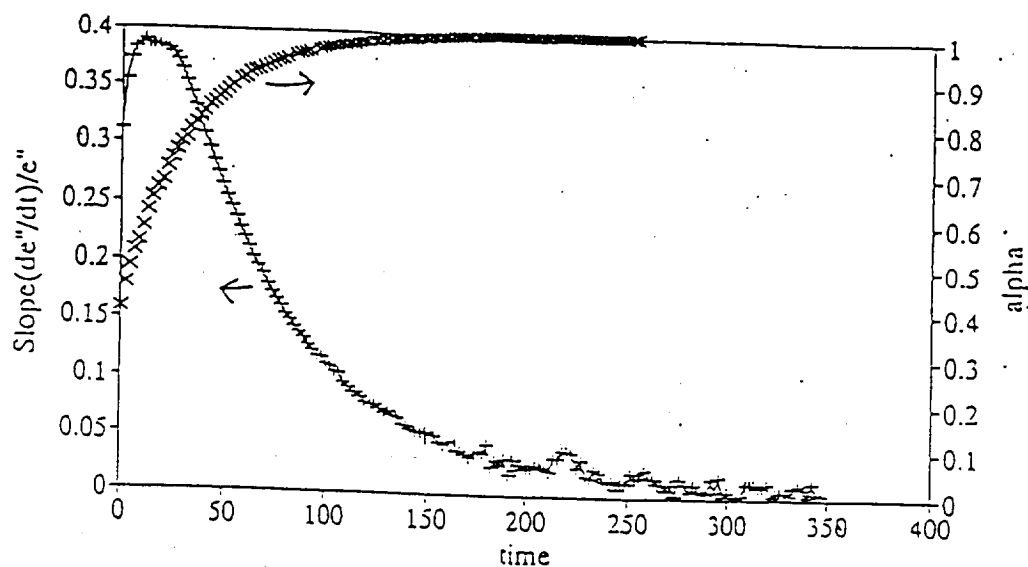


Figure 9. Correlation of $\frac{de''}{dt}/e''$ with time and degree of cure and with time showing sensitivity of normalized rate of change in ϵ'' to changes in final degree of cure near end reactions.

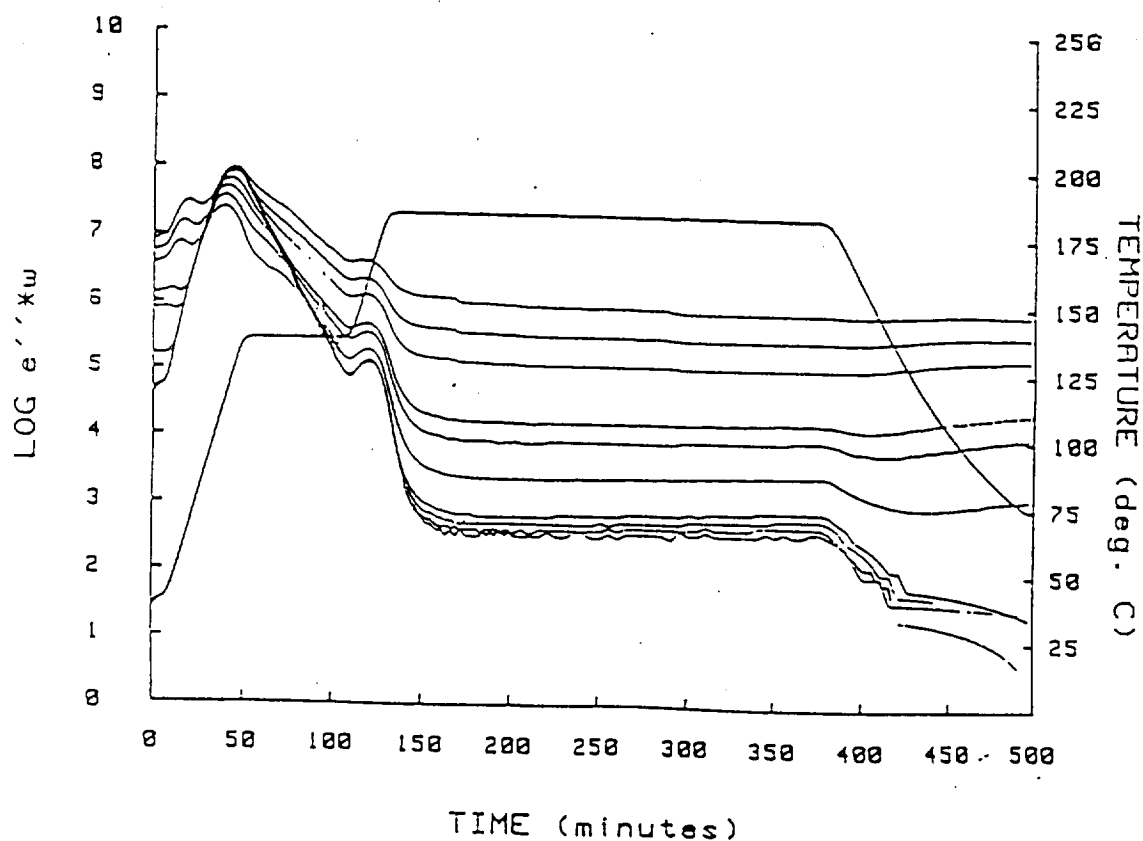


Figure 10. TGDDM epoxy cured in a press with a 135°, 177° cure cycle. Values of $\omega\epsilon''(\omega)$ are displayed for frequencies 1 MHz, 500, 250, 125, 50, 5 kHz, 500, 250, 125, 50 Hz (top to bottom).

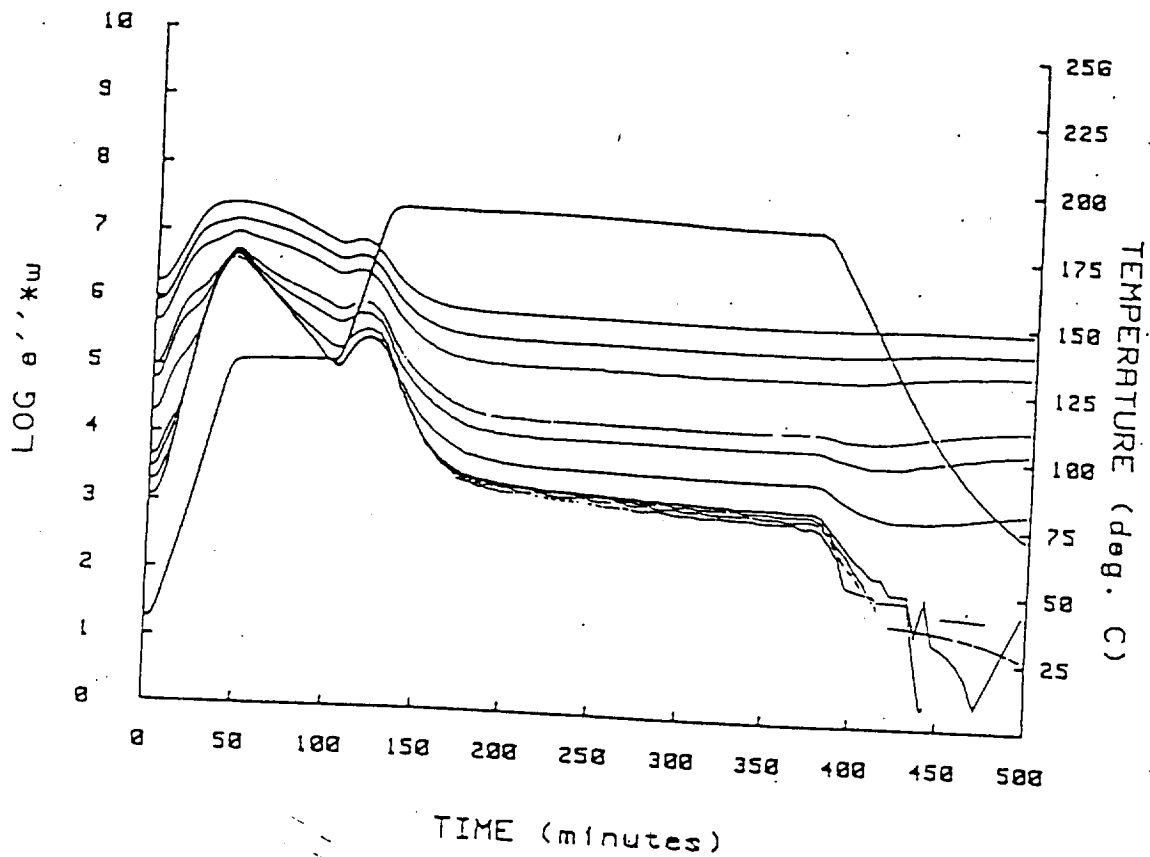


Figure 11. TGDDM epoxy which has been aged at room temperature for 30 days after which it is cured in a press using a 121°C intermediate hold.

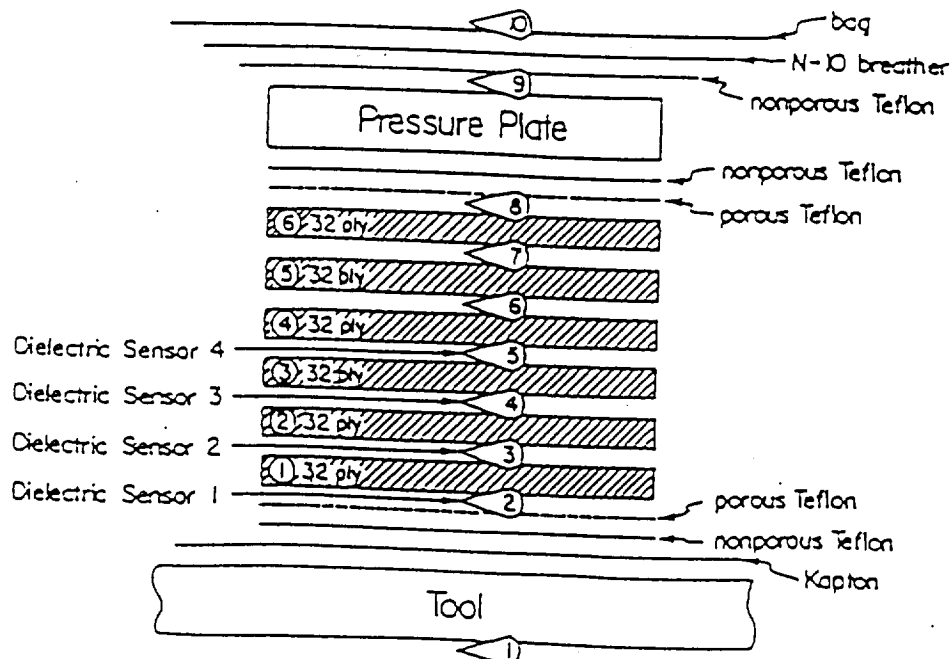


FIGURE 12. The layup of a thick TGDDM epoxy (Hercules 3501-6) graphite laminate autoclave run showing the positions of the dielectric sensors and thermocouples.

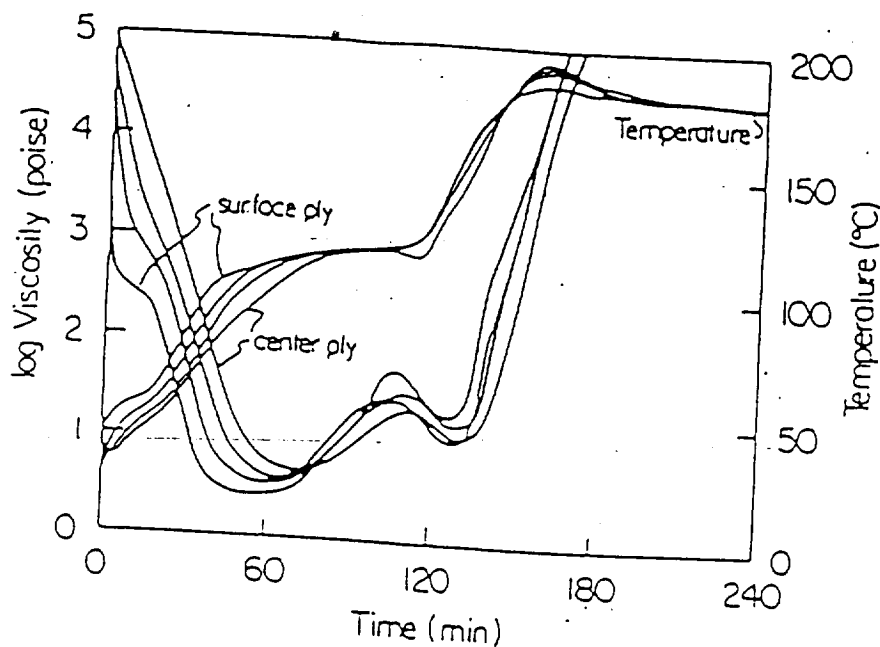


FIGURE 13 The viscosity of the thick laminate as determined from the frequency dependence of the FDEMS sensors at the surface, 32nd, 64th, and center plies.

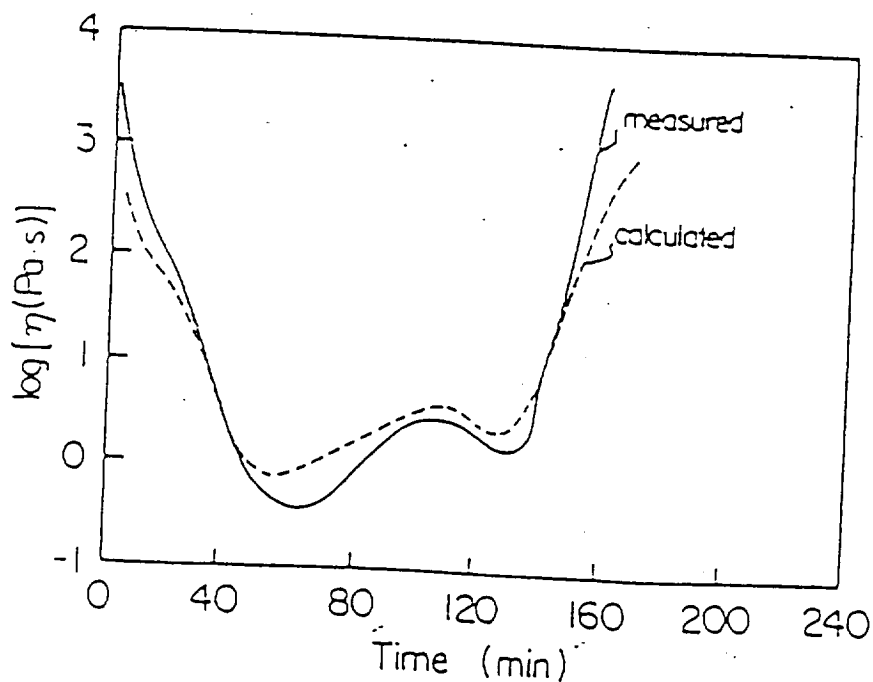


FIGURE 14 Comparison of the viscosity at the 64th ply as predicted by the FDEMS sensor and the Loos-Springer model.

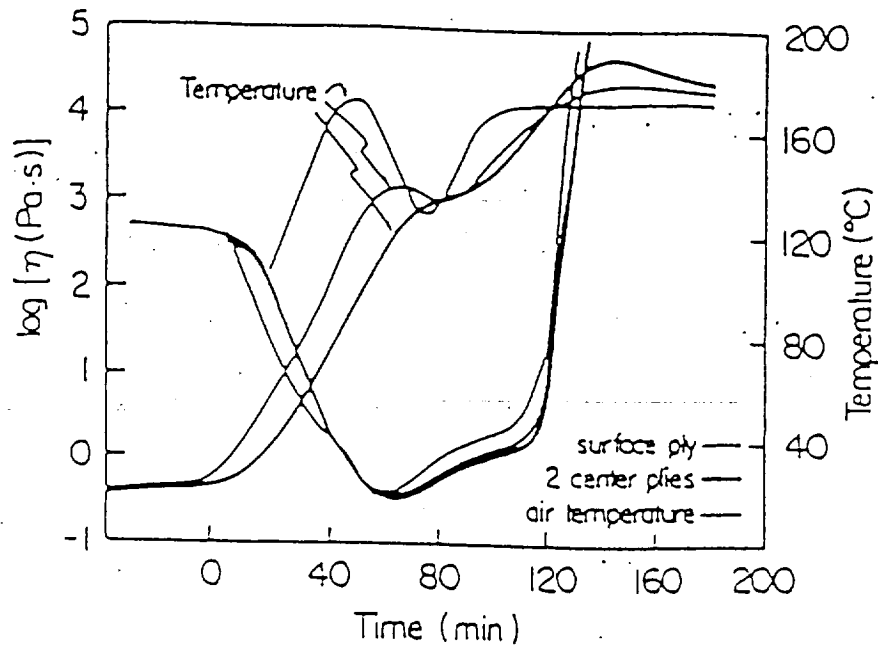


Figure 15 The viscosity at each sensor position of a 192-ply graphite-epoxy composite during a FDEMS sensor-controlled autoclave cure.

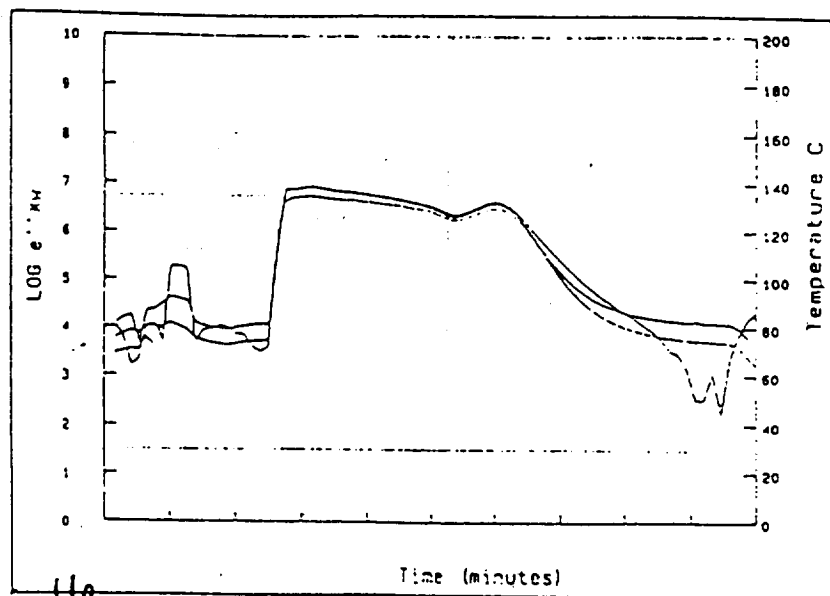


Figure 16 Output of $\omega\epsilon''(\omega)$ from sensor 1 (see Figure 1) for the MY720 aromatic TGMDA epoxy system commercially sold as 3501-6 by Hercules.

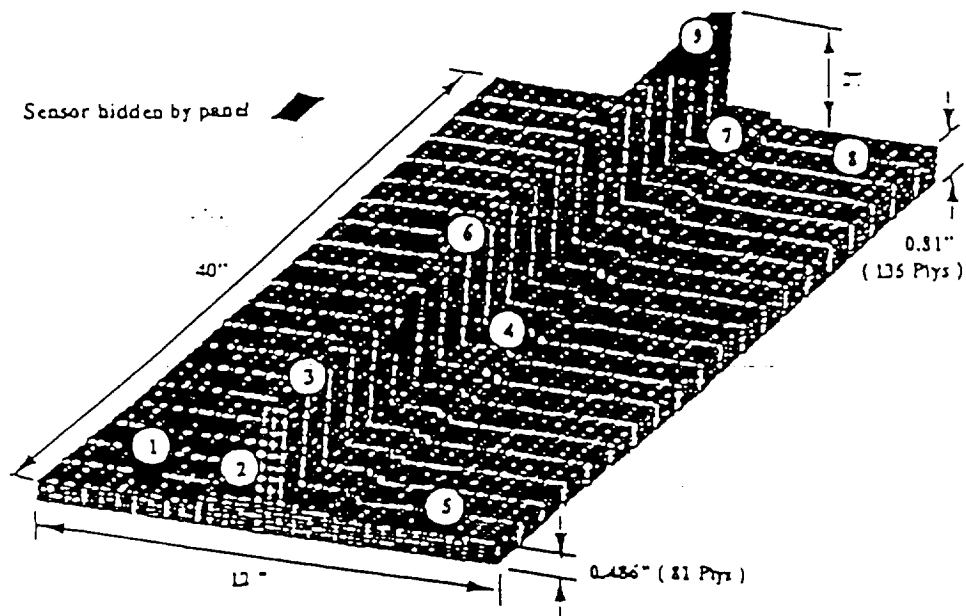


Figure 17 Locations of the 9 sensors monitoring position of the resin front viscosity and degree of cure in the T stiffened panel

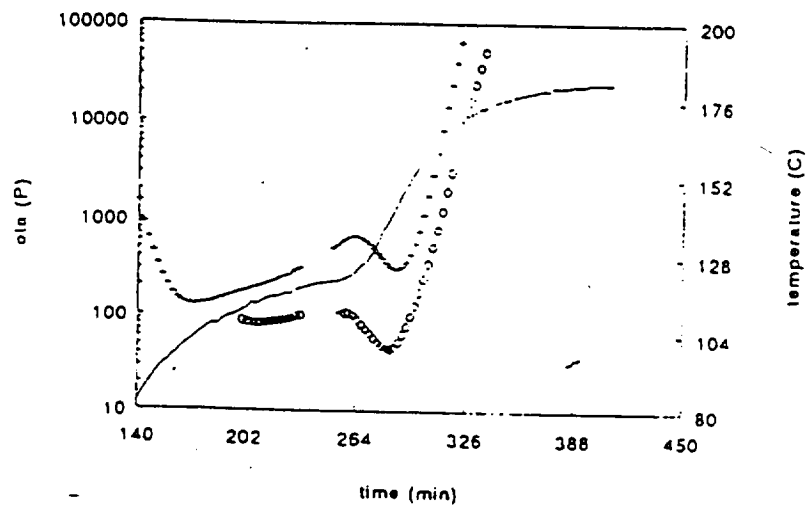


Figure 18 Viscosity of two different positions on the preform, position 1 on the flat panel and positions 3 at the top of the T stiffeners

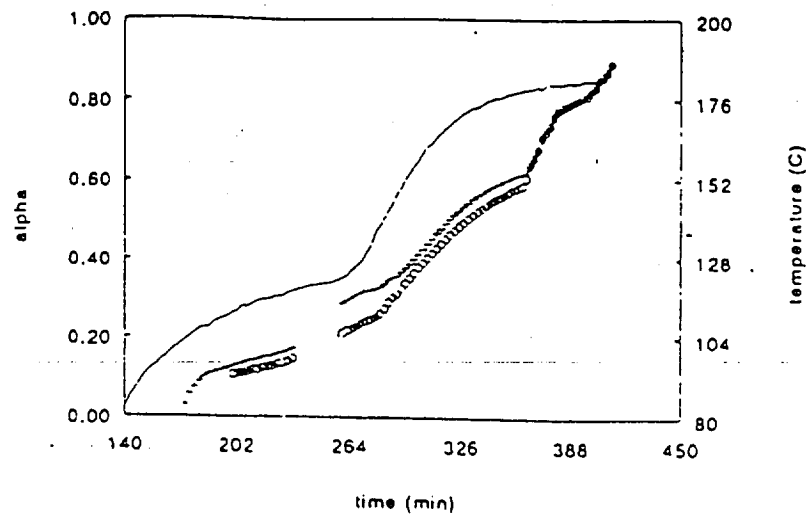


Figure 19 Degree of cure of two different positions on the preform, position 1 on the flat panel and position 3 at the top of the T stiffeners (see Figure 1).

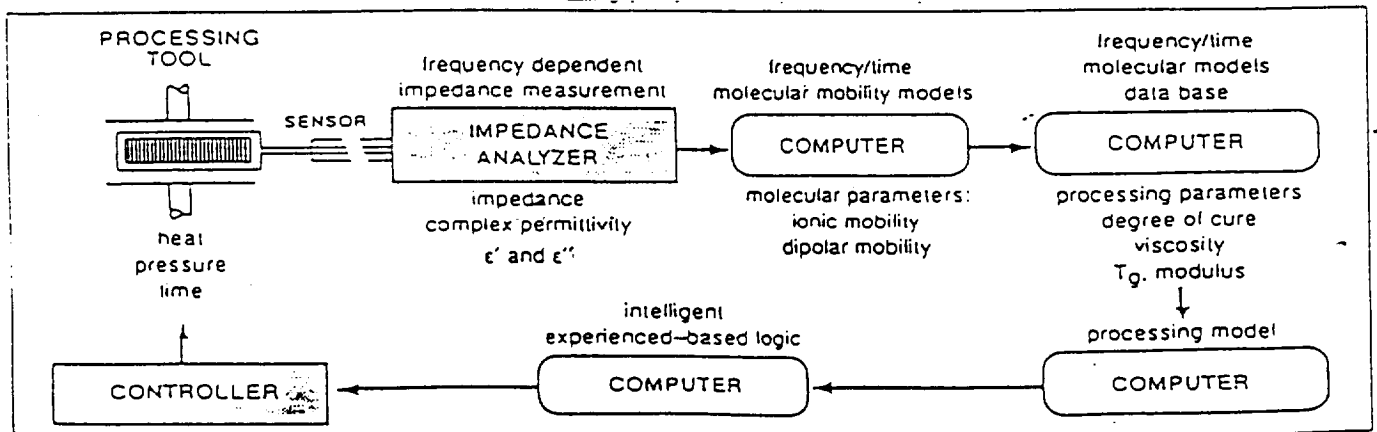


Figure 20 Schematic of the FDEMS sensor smart system for monitoring quality and for expert automated process control.

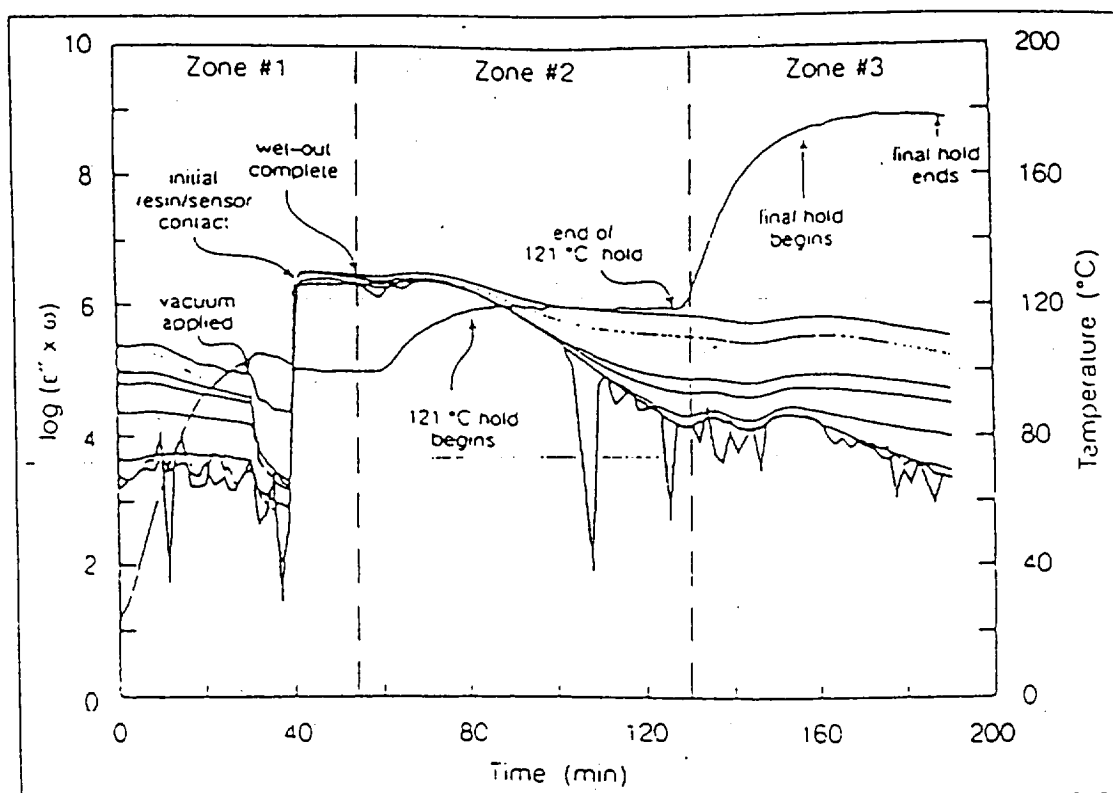


Figure 21 Sensor output for the smart automated sensor expert system-controlled run.