FINAL REPORT
NASA Grant NAG 1-1019

FDEMS Sensing for Automated Intelligent Processing of PMR-15

16 p.

David E. Kranbuehl
Chemistry and Applied Science
College of William and Mary
Williamsburg, Virginia 23187-8795
(757) 221-2542 (Tel) (757) 221-2542 (FAX)

SUMMARY

The purpose of this grant, which was done in conjunction with the Air Force, Phillips Laboratory in Edwards, California, was to develop FDEMS sensing to monitor and intelligently control the cure process in PMR-15. The project was teamed with Prof. Loos at VPI through a subcontract.

The enclosed article summarizes the successful completion of this work.

FDEMS SENSING FOR AUTOMATED INTELLIGENT PROCESSING OF POLYIMIDES

D. E. Kranbuehl, D. K. Hood, J. Rogozinski,
and R. Barksdale
Department of Chemistry
The College of William and Mary
Williamsburg, Virginia 23187-8795

Alfred C. Loos and Doug McRae
Department of Engineering Science and Mechanics
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

ABSTRACT

Frequency dependent dielectric measurements, often called frequency dependent electromagnetic sensing (FDEMS), made over many decades of frequency, Hz-MHz, provide a sensitive, convenient automated means for monitoring the processing properties of thermosets and thermoplastics. 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 detect chemical and physical changes throughout the entire cure process. In this presentation we will discuss using the frequency dependence in the Hz to MHz range to separate and determine parameters governing ionic and dipolar mobility. We will discuss the quantitative relationship of the ionic and dipolar mobility to monitoring processing parameters such as viscosity and degree of cure during the reaction.

We will show applications of in situ FDEMS sensing for closed loop intelligent process control of the cure of a high temperature polyimide and a high performance epoxy. The insitu cure monitoring sensor has been developed and incorporated into an automated closed loop sure control system to control cure. The sensor system combines Frequency Dependent Electromagnetic Sensing (FDEMS), results from the Loos Processing Model, and the Abrams Qualitative Process Automation Language (QPAL). The sensor system is able to respond to material and process variability due to aging, intra and interbatch variations, moisture absorption during storage, tool heat transfer phenomena and differences in resins. It has been used to control the cure of PMR-15.

1. INTRODUCTION

The FDEMS-Loos Model-QPALS intelligent automated cure control system developed at William and Mary has been used to process fresh and aged PMR-15/graphite and fresh AFR-700/graphite polyimide prepreg materials. By responding on a molecular level to prepreg variations resulting from resin or batch variation, aging and/or moisture absorption and tool heat transfer phenomena, the sensor-model expert system is capable of successfully processing materials which may not be processable using a strict time temperature recipe approach. The coupling of in situ Frequency Dependent Electromagnetic Sensing (FDEMS) measurements with Qualitative Process Automation Language (QPAL) knowledge base containing the material process goals created from the results of the Loos processing model, manufacturer recommendation and prior experimentation allows the expert system to optimize in real time the ongoing cure process.

Conventionally formulated PMR-15 is a stoichiometric mixture of the nadic ester of 5-norbornene-2,3-dicarboxylate (NE), the dimethyl ester of 3,3',4,4' -benzophenone tetracarboxylate (BTDE) and 4,4'-methylendianiline (MDA) in the monomer ratio 2(NE):(n+1)MDA:n(BTDE) where n = 2.087 (Serafini, 1972) (Hoy, 1988). Previous work has discussed resin variation as a function of incidental hydrolysis, esterification, and oligomer formation in PMR-15 (Kranbuehl, 1986 and 1991) and the results of our earlier work on intelligent expert cure of PMR-15/graphite composites (Hart, 1992 and 1993).

AFR-700 has been developed to be the next generation polyimide resin for high performance graphite composites. It has been designed for **use** temperatures exceeding those of PMR-15 (*circa* 300°C) with similar processability.

Earlier studies including Gluyas (1976), Kranbuehl, (1989 and 1990), Ciriscioli (1990) and Sheppard (1990) have shown that in situ dielectric measurements can provide a convenient method for monitoring the cure of a variety of resins, including PMR-15 and AFR-700. This work focuses on using FDEMS sensing for automated intelligent process control.

2. FDEMS THEORY

Measurements are made of the capacitance, C, and conductance, G, using the Dek Dyne microsensor. The complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ was calculated from:

$$\varepsilon' = \frac{C\ material}{C_0} \qquad (1)$$

and

$$\epsilon'' = \frac{G\ material}{C_0 2\pi f} \qquad (2)$$

at each of 9 frequencies between 125 Hz and 1 MHz. This calculation is possible when using the Dek Dyne microsensor whose geometry independent capitance, C_o, is invariant over all measurement conditions.

Both the real and the imaginary parts of ε^* have an ionic and dipolar component. The dipolar component arises from diffusion of bound charge or molecular dipole moments. The dipolar term is generally the major component of the dielectric signal at high frequencies and in highly viscous media. The ionic component generally dominates ε^* at low frequencies, low viscosities and/or higher temperatures.

Simultaneous measurement of the frequency dependence of both ε' and ε'', or C and G, in the Hz to MHz range is, in general, optimum for determining both the ionic mobility or conductivity, σ, and a mean dipolar relaxation time, τ. These two parameters are directly related on a molecular level to the rate of ionic translational diffusion and dipolar rotational mobility and thereby to changes in the molecular structure of the resin which reflect the reaction rate, changes in viscosity/modulus and changes in the degree of cure.

Plots of the product of frequency (ε) multiplied by the imaginary component of the component of the complex permittivity $\varepsilon''(\omega)$ 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 $\omega\varepsilon''(\omega)$ can be used to measure the change with time of the ionic mobility through the parameter σ where

$$\sigma(ohm^{-1}cm^{-1}) = \epsilon_0 \omega \epsilon_i''(\omega) \qquad (3)$$

$$\epsilon_0 = 8.854 \times 10^{-14} C^2 J^{-1} cm^{-1}$$

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.

The peaks in ω'' 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 $\varepsilon''(\omega)$ 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 $\frac{de''}{dt}/e''$ can be used to monitor insitu 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.

3. QUALITATIVE PROCESS AUTOMATION LANGUAGE (QPAL)

QPAL, developed cooperatively by Wright-Patterson Air Force Base, Ohio, and Lawrence Associates, Dayton, Ohio, is a highly structured Macintosh™ programming language that has been tailored for polymer cure processing. The use of QPAL in an expert control system provides three distinct advantages. First, complicated, and often conflicting, goals for the composite fabrication process are reduced to a series of discrete steps, or episodes, which define the desired cure process. Another advantage is the portability of a given resin specific knowledge base, with minor modifications, to other expert control systems also using QPAL. Finally, QPAL is capable of testing a newly modified knowledge base either internally through a user defined trace or externally from previously obtained experimental FDEMS/temperature data without having to run a series of time consuming and expensive composite fabrication runs (12).

4. EXPERIMENTAL

PMR-15/graphite prepreg, provided by ICI Fiberite, and AFR700/graphite prepreg, provided by Hughes Aircraft, have been used to make flat composite panels ranging in thickness of less than 1/8 inch to 1/4 inch. Various fresh and aged prepreg samples have been used. Aged materials have been stored for discrete periods of time under everyday freezer storage conditions.

FDEMS measurements are made over the range of frequencies from 125 Hz to 1 MHz using a Dek Dyne FDEMS microsensor. The microsensor consists of a fine array of two interdigitated comb electrodes on a ceramic substrate. It is inert, disposable, planar, and geometry independent. The sensor is constructed of noble metals and high temperature ceramics and contains no solid state circuitry which is vulnerable to harsh processing environments. The sensor can withstand the oxidative conditions and tool temperature and pressures for cure conditions exceeding 400°C and 1 MPa. This single disposable sensor monitors simultaneously the entire range in magnitude (usually 10^{-2} to 10^{8}) of both the real ε' and imaginary ε'' components of the permittivity continuously throughout the cure process.

5. RESULTS AND DISCUSSION

Figure 1 shows the FDEMS output for a "typical" fresh PMR-15 prepreg (ICI Fiberite Lot #10502S) cure using a time-temperature profile that incorporates the results of our previous work. Region A shows FDEMS sensor wet-out on a slow 2°C/minute ramp to 80°C and the achievement of a viscosity minimum for the system. Region B is a one hour hold at 80°C to allow for solvent elution and maximum part wet-out. Region C shows

the onset of imidization as characterized by a drop in resin fluidity. Region D shows the continuation of the imidization reaction during a one hour hold at 200°C. Normally one would want to hold until the imidization is complete as evidenced by the decrease in the slope of the FDEMS signal; that is, $((d\varepsilon''/dt)/\varepsilon'')$ approaching zero. Here we see that the use of sensor feedback would have shown the imidization reaction to be incomplete and therefore the hold would have been extended by the intelligent, automated cure control system. Regions E and F show the viscosity minimum achieved during a ramp to 265°C and the subsequent decrease in FDEMS signal as residual solvent and other volatiles are eluted during the hold. Finally, Regions G and H show the ramp to and hold at 320°C, the final crosslinking hold. Note that after approximately 75 minutes in the 320°C hold the change in slope of ε'', $((d\varepsilon''/dt)/\varepsilon'')$, is small and close to zero, and 'full cure' based on user criteria is reached. Had our intelligent, automated cure control system controlled this run using the criterion of $((d\varepsilon''/dt)/\varepsilon'') \leq 3.0 \times 10^{-5}$, it could have terminated the run after a total cure time of 375 minutes, thus saving 105 minutes of the 480 minutes shown here.

Figure 2 shows the dielectric and temperature output for the intelligent sensor-model automated cure of a different lot of fresh PMR-15 prepreg (ICI Fiberite Lot #11769S). Region A shows the panel as it warms from room temperature to approximately 80°C. FDEMS sensor wet out is indicated by the sharp increase in the Log $(\varepsilon''*\omega)$ signal at 81°C. Note that the max in Log $(\varepsilon''*\omega)$ for the prepreg sample is almost 1 decade lower than that seen for prepreg Lot #10502S in Figure 1. Region B, Imidization Onset, is a hold near 80°C to allow for solvent elution prior to beginning a slow ramp to the imidization hold temperature. Region B requires that the magnitude of Log $(\varepsilon''*\omega)$ at 500 Hz, 5 kHz, and 25 kHz be less than 8.0 for four consecutive readings, that the change in FDEMS signal at 25 kHz, $((d\varepsilon''/dt)/\varepsilon'')$, be decreasing (*i.e.*, negative) for four consecutive cycles, and that the magnitude of Log $(\varepsilon''*\omega)$ at 25 kHz decrease by ten percent from the maximum value determined at the beginning of the hold. Based on these criteria, Region B is an eleven minute hold at 81°C. Region C is the slow 2-3°C per minute ramp to the 200°C hold temperature. Region D shows the imidization hold at 200°C lasting for only twelve minutes before meeting the criterion that the value of $((d\varepsilon''/dt)/\varepsilon'')$ at 25 kHz be less than 3 x 104 for four consecutive data acquisition cycles. This short dwell time indicates the virtual completion of the imidization reaction prior to entering Imidization Hold. Obviously, then, the required 1 hour hold seen in Region D of Figure 1 would have been wasted processing time for this composite cure. Regions E and F are the ramp to the minimum viscosity consolidation temperature and the preset 30 minute hold at that temperature, respectively. The knowledge base determined the minimum viscosity temperature for this run to be 260°C based on the criterion that the ionic conductivity of the resin be decreasing (*i.e.*, the Log $(\varepsilon''*\omega)$ signal is folding over, a temperature that is quite close to the optimal model generated 265°C compaction temperature seen in Figure 1. Finally, Region G shows the slow ramp to the 320°C final crosslinking cure temperature and Region H shows the achievement of full cure, based on the criterion that $((d\varepsilon''/dt)/\varepsilon'')$ at 25 kHz be less than 3 x 105 for four consecutive data acquisition cycles, after 115 minutes. Regions I and J show system cool down and shut down, respectively. The total cure time for this fresh PMR-15 prepreg processing run was 338 minutes. Thus we see that resin/prepreg batch variability significantly affect the way a given 'standard' material will process.

Figures 3a and 3b show the FDEMS output for the intelligent sensor model cure of a

third sample of fresh PMR-15/graphite prepreg (ICI Fiberite Lot #10645S). A careful analysis of the data shows the expected variations in optimized time temperature cure profile resulting from resin/prepreg batch variation and the significant effects of poor tool heat transfer phenomena. In Figure 3a, the PMR-15 matrix resin achieves maximum flow at 82°C, a value comparable to that found in Figure 2 as well as in previous results (12-14). Region B, Imidization Onset, shows the loss of solvent during a 79 minute hold near the minimum viscosity temperature. The criteria for this optimized cure required the FDEMS signal $((d\varepsilon''/dt)/\varepsilon'')$ to be decreasing and the value of Log $(\varepsilon''*\omega)$ at 25 kHz to be less than 5.5 for four consecutive data acquisition cycles. Region C shows the Imidization Ramp to 200°C and Region D the Imidization Hold at that temperature. Note that the Imidization Hold lasted only 10 minutes, signifying the completion of the majority of the imidization process prior to reaching 200°C as was also seen in Figure 2. Region E shows the determination of the crosslinking Min Viscosity temperature at 255°C, well below the Loos PMR-15 processing model-based optimal 265°C. Again we see the value of monitoring the resin state on the molecular level in order to optimize the achievement of the 'ideal' processing milestones. Region F is the 44 minute hold needed to achieve part consolidation and residual volatile evolution. Figure 3b, Region G is the ramp to 320°C and Region H is the Final 3~ Cure Hold. Note that the 205 minutes necessary to meet the final cure criterion of $((d\varepsilon''/dt)/\varepsilon'') \leq 3 \times 10^{-5}$ at 25 kHz for four consecutive readings is 90 minutes longer than the time required for the Lot #11769S prepreg to achieve the same defined 'full cure'.

Additionally, these figures also show the significance that poor tool heat transfer can have on total processing time, and thus fabrication cost. In Region A it took the temperature at the middle ply of the part (shown for all figures) 100 minutes to increase from room temperature to 82°C. Although the normal ramp rate would be 2-4°C/minute, the intelligent cure control system reduced the overall rate to approximately 0.5°C/minute due to the several thermal gradients which existed between the part and thermal press set temperatures. In Region C we again note the part temperature increasing at a very slow 0.5°C/minute due to poor tool to part heat transfer. What ideally should have taken approximately 30 and 70 minutes to occur in Regions A and C, respectively, required over three times the expected length of time in each case. Had the heating process been only time dependent, it is very likely that a void rich, useless composite would have resulted. Thus we see the importance of using the expert system to control the cure of composite parts.

Figure 4 shows the FDEMS data for a PMR-15/graphite prepreg sample aged 7 months under freezer conditions (ICI Fiberite Lot #10502S). The labelled zones correspond to those previously described. Comparisons with the dielectric and temperature data for the optimized cures of fresh PMR-15 prepreg seen in Figures 2-4, show several significant differences as a result of the aging process. In Region A, the viscosity minimum defined by the maximum in Log $(\varepsilon''*\omega)$ at 25 kHz occurred at 8.5, one decade higher than was seen for the expertly cured fresh PMR-15/graphite prepreg. In fact, the low frequency Log $(\varepsilon''*\omega)$ lines at 125, 250 and 500 Hz lie below the overlapping ionic frequency band seen centered around Region B. This phenomenon results from charge polarization effects which are significant only in highly fluid systems and is indicative of water absorption during the aging process. Region B, Imidization Onset, was a 30 minute hold at the intelligently determined minimum viscosity temperature of 83°C. Region D, the Imidization Hold, lasted only 4 minutes, the minimum time necessary to meet the criterion that the dielectric signal $((d\varepsilon''/dt)/\varepsilon'') \leq 3.0 \times 10^{-4}$ at 25 kHz for four consecutive data acquisition cycles thus signifying completion of the imidization process. This

result is indicative of the advancement of the reaction processes leading to complete imidization as a function of the aging process. The third major indicator of material variability is the minimum viscosity consolidation temperature determined by the sensor-model intelligent cure control system in Region E. For this 7 month freezer aged PMR-15 prepreg, this Crosslinking Min Viscosity temperature, as determined by the normalized decrease, or 'folding over' in the FDEMS signal occurred at 290°C. This 25°C increase from the model determined 265°C optimized softening temperature again seems to indicate that the prepreg has aged considerably. Region H, the Final Cure Hold at 320°C, requires only 75 minutes to meet the 'cure complete' criterion that $((d\varepsilon''/dt)/\varepsilon'') \leq 3.0 \times 10^{-5}$ at 25 kHz for 4 consecutive data acquisition cycles. This hold time was much shorter than those seen for the prepreg materials in Figures 1-4, the final indicator of the age of the starting prepreg.

Figure 5 shows the application of the described PMR-15 QPAL knowledge base for the expert cure of fresh AFR-700/graphite prepreg. In Region A the AFR-700 resin reaches its viscosity minimum at 72°C with a magnitude of 9.1 in the Log ($\varepsilon''*\omega$) FDEMS signal. This high dielectric signal (low viscosity) at a low temperature indicates the potential for better fiber wet out by the AFR-700 matrix resin when compared to PMR-15. Region B shows the loss of volatiles during a nominal hold as the maximum flow temperature. The continuous rise in temperature observed resulted from the thermal lag of the part behind the temperature set point of the thermal press. Region C shows the 2-3°C/minute Imidization Ramp to the 200°C Imidization Hold as seen in Region D. This hold required 90 minutes for the imidization process to reach completion as determined by the changes in FDEMS signal ($(d\varepsilon''/dt)/\varepsilon''$) at 25 kHz being less than 3.0×10^{-4} for four consecutive data acquisition cycles. Region E shows the determination of the Crosslinking Min Viscosity temperature for part consolidation based on the decrease, or 'folding over', in dielectric signal at 296°C. This high temperature indicates that the AFR-700 polymer has achieved a degree of chain interaction by the end of the imidization process that is higher than that seen with fresh PMR-15 prepreg samples. The Region F Crosslinking Hold to allow for volatile evolution and part compaction needed 90 minutes of 296°C to achieve the requirement that ($(d\varepsilon''/dt)/\varepsilon''$) at 25 kHz be less than 3.0×10^{-4} for four consecutive expert process cycles. Region G shows the ramp to the Region H Final Cure Hold temperature of 320°C. This hold terminated by reaching the maximum allowed hold time of 240 minutes. This would seem to indicate that the PMR15 criterion that the change in FDEMS signal ($(d\varepsilon''/dt)/\varepsilon''$) at 25 kHz $\leq 3.0 \times 10^{-5}$ for four consecutive data acquisition cycles may not be appropriate for AFR700. Region I shows part/tool cool down and Region J shows sensor-model intelligent cure control system shutdown.

6. CONCLUSIONS

The FDEMS-Loos Model-QPALS intelligent, automated closed loop cure control system has been developed and used to control the cure of polyimides. The expert system combines in situ Frequency Dependent Electromagnetic Sensing, results from the Loos Processing Model for PMR-15, and the Qualitative Process Automation Language. The QPAL logic shell and the user defined knowledge base provides a flexible environment in which to compare the real time FDEMS data regarding the microscopic state of the material with the model and experimentally generated process goals. The expert system responds in real time to material variability as a function of batch variations, aging, incidental moisture absorption, tool heat

transfer phenomena and differences in matrix resin systems.

7. ACKNOWLEDGEMENT

This work was made possible through the support of the NSF Center for High Performance Adhesives and Composites at Virginia Polytechnic Institute and State University, Blacksburg, Virginia, NSF #DMR91-2004, the Phillips Laboratory, Edwards Air Force Base, California, and the National Aeronautics and Space Administration Langley Research Center, Hampton, Virginia.

*Inquiries regarding the FDEMS sensor/instrumentation and the expert system should be directed to D. Kranbuehl.

8. REFERENCES

Ciriscioli, P., Q. Wang and G. Springer, Int. SAMPE Symp. Ser. **35**, 1507-1516 (1990).

Gluyas, R. E.,NASA TM X-73448 (1976).

Hart, S., D. Kranbuehl, A. Loos, B. Hinds, J. Koury and J. Harvey, Int. SAMPE Symp. Ser. **38** (1), 1009-1019 (1993).

Hay, J., J. Boyle, J. Walton and D. Wilson, 3rd Int. Conf. on Polyimides (1988).

Kranbuehl, D., *Cure Monitoring*, Encyclopedia of Composites, S. M. Lee, ed., VCH Publishers, 531-543 (1990).

Kranbuehl, D., S. Delos and P. Jue, *Polymer* **27**, 11 (1986).

Kranbuehl, D., D. Eichinger, D. Rice, H. Tully and J. Koury, Int. SAMPE Symp. Ser. **34** (1), 79 (1989).

Kranbuehl, D., T. Prettyman, K. Robillard, A. Loos and J. Koury, Int. SAMPE Symp. **36**, 1161-1167 (1991).

Serafini, T. T., P. Delrigs and G. R. Lightsey, *J. Appl. Pol. Sci.* **16**, 904 (1972).

Sheppard, D., Int. SAMPE Symp. Ser. **35**, 1499-1506 (1990).

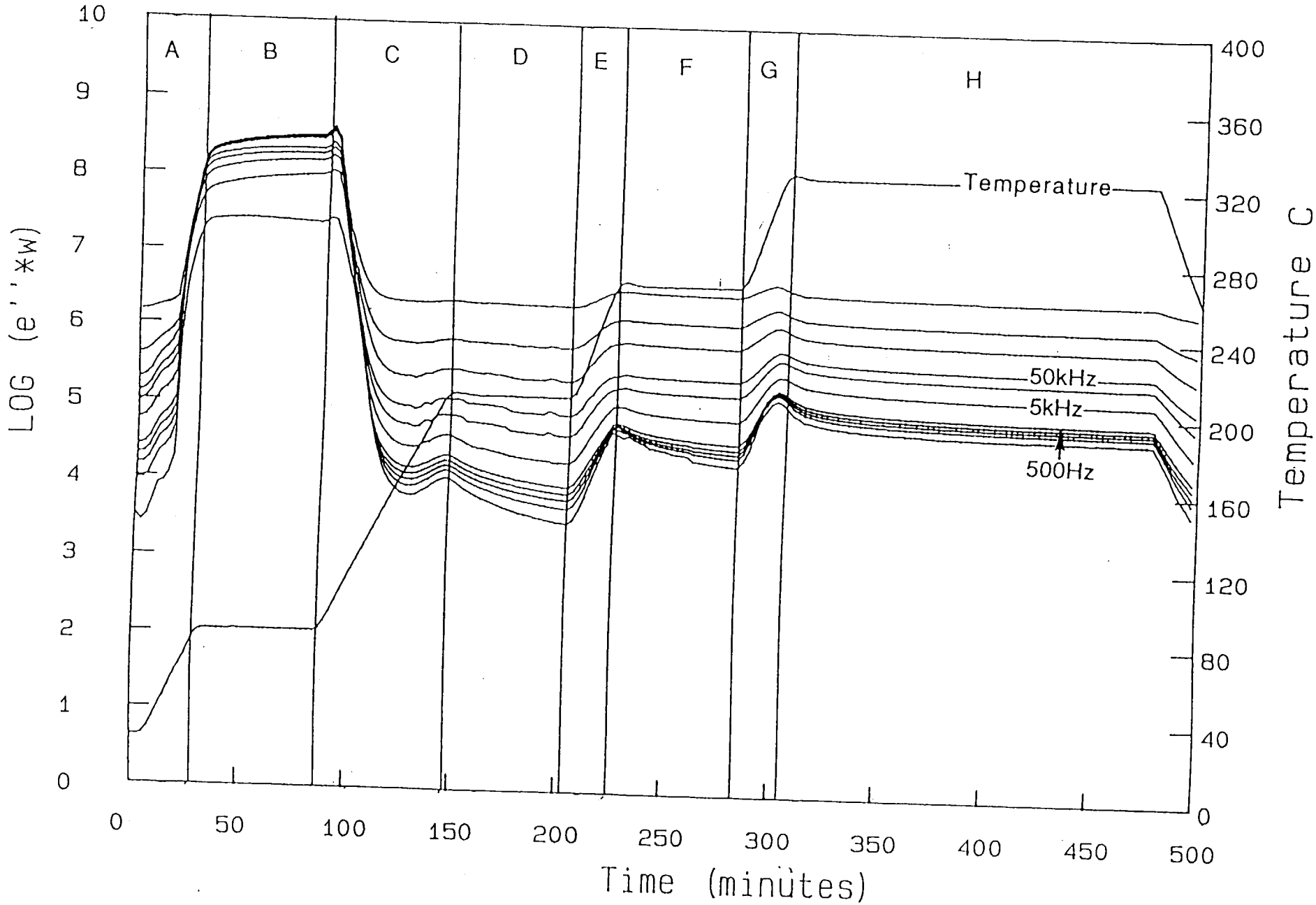

Figure 1 Values of temperature and ε'' multiplied by frequency for a "standard" cure of fresh PMR-15 prepreg. (Lot #10502S)

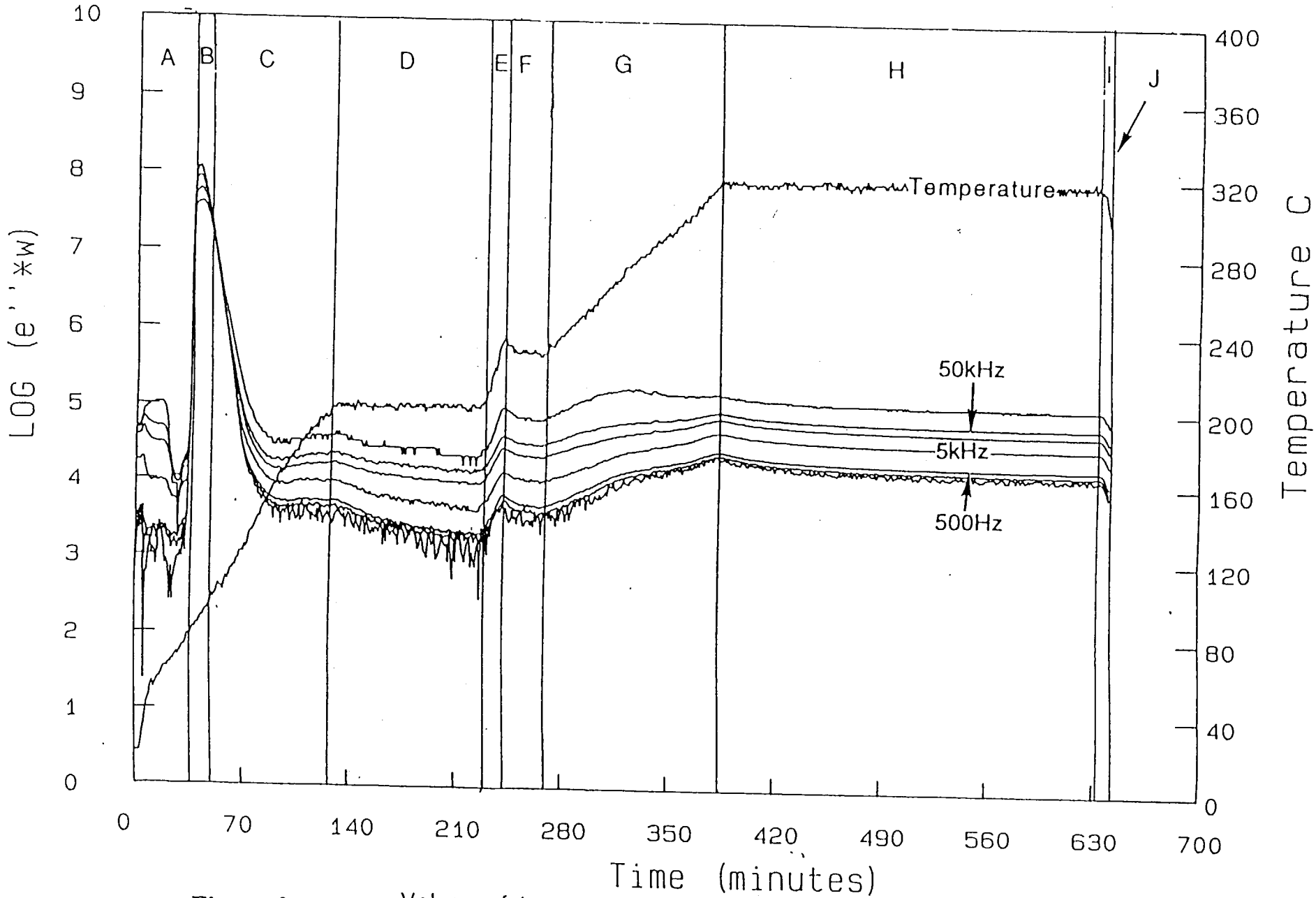

Figure 2 Values of temperature and ε" multiplied by frequency for an intelligent, automated cure of fresh PMR-15 prepreg. (Lot #11769S)

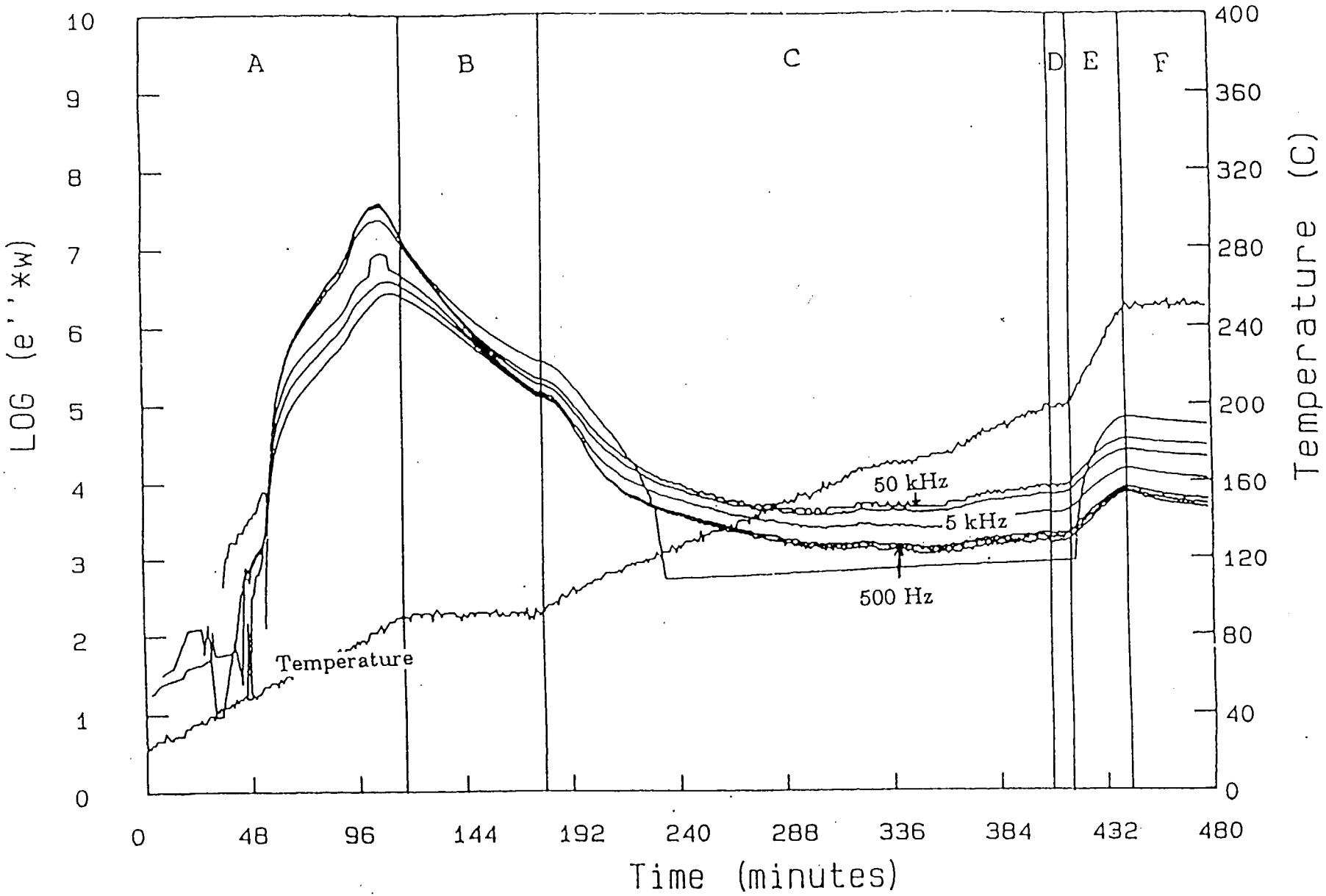

Figure 3a Values of temperature and ε″ multiplied by frequency for a sensor-model intelligent automated cure of a second batch of fresh PMR-15 prepreg. (Lot #10645S)

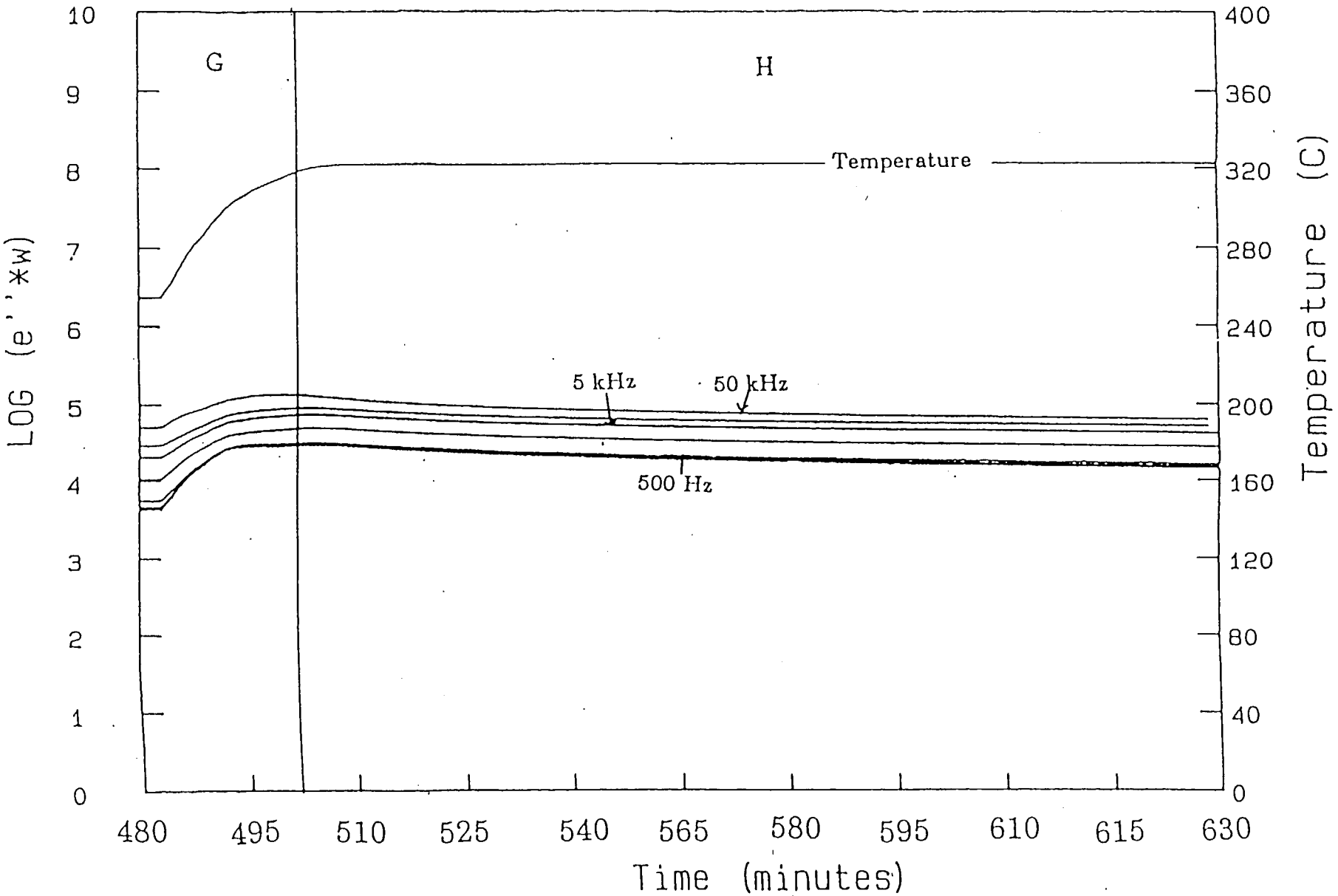

Figure 3b Continuation of the temperature and ε″ multiplied by frequency expert cure data for the Lot #10645S fresh PMR-15 prepreg.

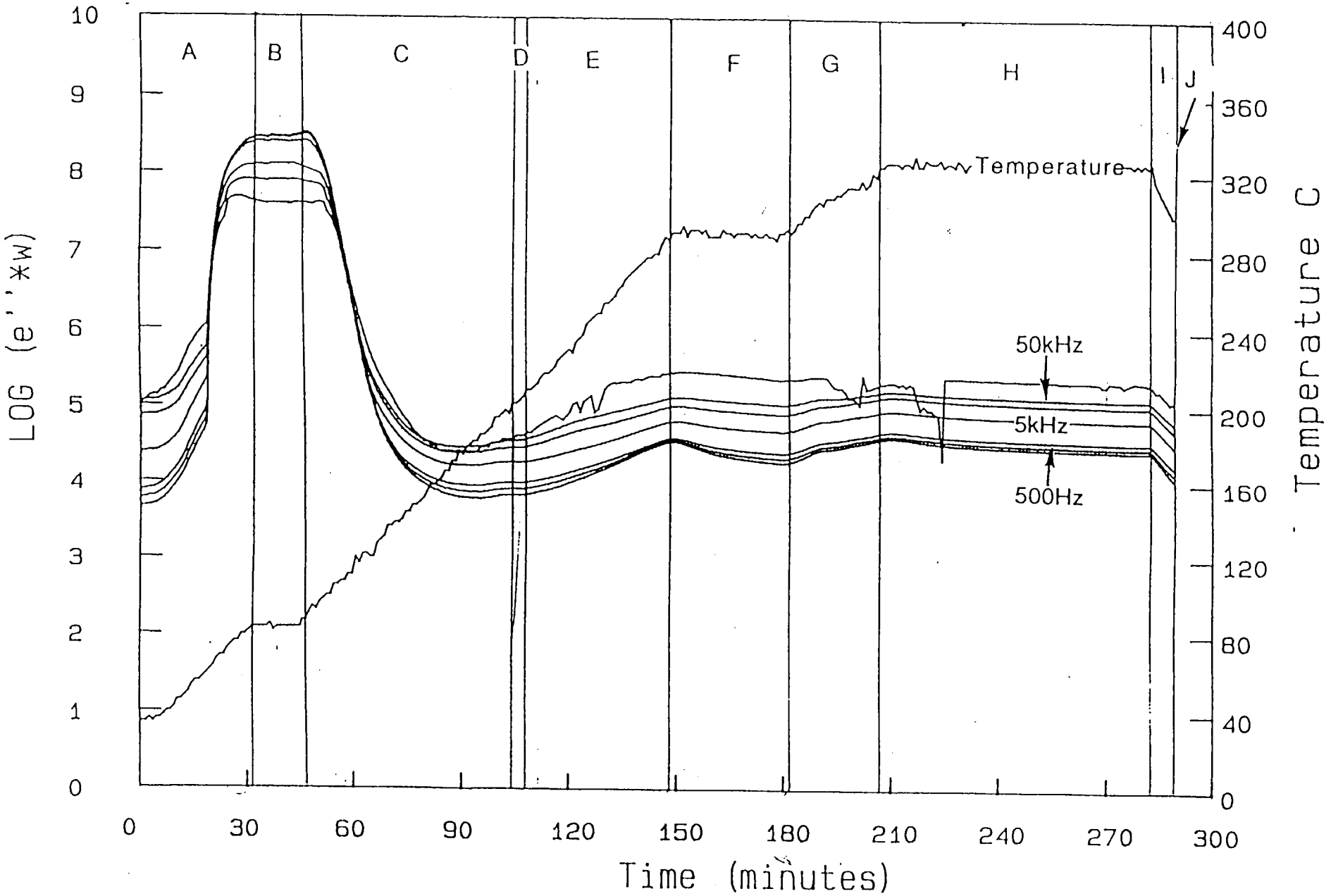

Figure 4 Values of temperature and ε'' multiplied by frequency for an intelligent, automated cure of PMR-15 prepreg aged seven months under freezer conditions. (Lot #10502S)

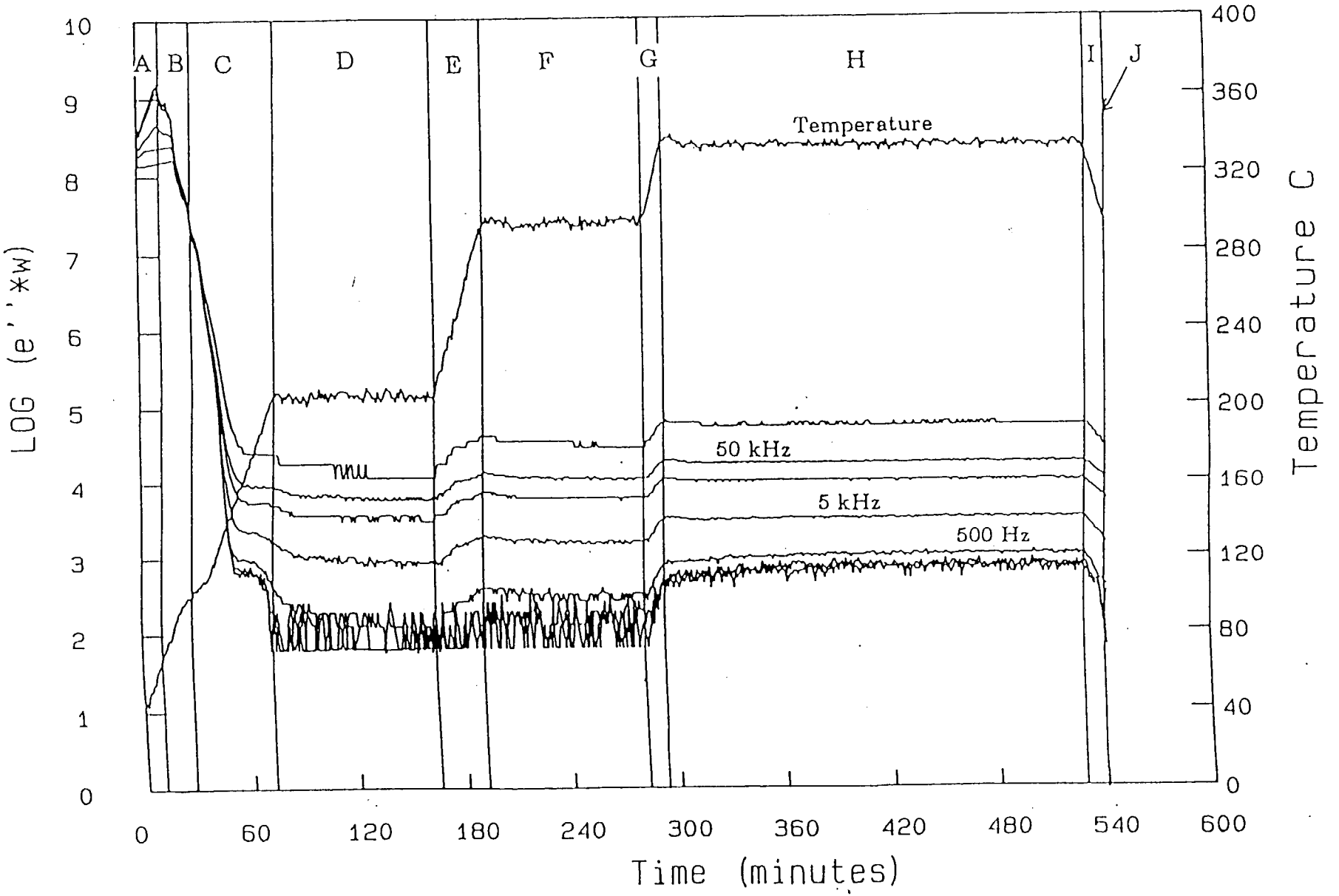

Figure 5 Values of temperature and ε″ multiplied by frequency for the sensor-model intelligent automated cure of fresh AFR-700 prepreg using the PMR-15 polyimide QPAL knowledge base.