

DYNAMIC DIELECTRIC ANALYSIS FOR NONDESTRUCTIVE

CURE MONITORING AND PROCESS CONTROL

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INTRODUCTION

Dynamic dielectric analysis (DDA) is an instrumental means for quantitative material evaluation and closed loop "smart" cure cycle control. DDA is particularly important to process control because it is one of only a few experimental techniques for conveniently studying the cure process continuously, that is, to examine the cure chemistry throughout the process of going from a monomeric liquid of varying viscosity to a crosslinked, insoluble, high temperature solid [1-3]. The key for achieving this goal is to relate the chemistry of the cure process to the dielectric properties of the polymer system by correlating time, temperature and frequency dependent dielectric measurements with other chemical characterization methods.

The frequency dependence of the DDA measurement of ϵ^* is used to isolate and characterize ionic translational diffusion and dipolar rotational diffusion. This molecular information provides a means for monitoring the course of the reaction and the viscosity. From the frequency dependence of the dielectric loss, a specific conductivity is calculated which, in turn, is related to the extent of reaction.

Dielectric characterization measurements have been made on aromatic polyimide, epoxy, and thermoplastic resin systems. DDA is used to monitor reaction progress, the effect of age and moisture, and thermoplastic phase changes. It is also shown to be an effective in-situ method for monitoring viscosity and relative degree of cure within a thick laminate.

EXPERIMENTAL

Dynamic dielectric measurements were made using a Hewlett-Packard 4192A LF Impedance Analyzer controlled by a 9826 Hewlett-Packard computer. The resin was cured in a 3" mold placed between thermostated heating plates or in an autoclave. The time-temperature profile of the mold was controlled by a program in the computer. The layup consisted of a number of layers of Kapton to insulate the sensor from the metal mold, a geometry-independent Dek Dyne sensor* which can be inserted directly between layers of polymer resin and further layers of Kapton between

this and the mold top. An iron-Constantan thermocouple was placed next to each dielectric sensor and the temperature measured by a Keithley 179 TRMS Digital Multimeter.

Measurements of capacitance (C) and conductance (G) at frequencies from 5 to 5×10^6 Hz were taken at regular intervals during the cure cycle and stored on a computer disk. The complex permittivity was calculated for each of these measurements. The temperature was also recorded for each measurement. Plots of the results were prepared from the stored data and were plotted using a Hewlett-Packard 7475A 6 pen plotter. The simultaneous viscosity, acoustic and dielectric measurements were made in a Rheometrics System 4 Rheometer equipped with a specially designed accessory containing the sensors for all 3 experiments. Ultrasonic measurements were made using a pulse echo apparatus (5MHz) [4]. The resins used in these studies were obtained from the following sources:

a thermosetting polyimide (PMR-15)	General Electric
a thermoplastic polyimide (LaRC-TPI)	NASA-Langley Research Center
poly (arylene ether) (PAE)	NASA-Langley Research Center
poly (ether ether keton) (PEEK)	NASA-Langley Research Center
a tetraglycidyl diaminodiphenyl methane based epoxy (Hercules 3501-6)	NASA-Langley Research Center

All materials were sealed and stored in a freezer until used.

THEORY

Measurements of C and G were used to calculate the complex permittivity, $\epsilon^* = \epsilon' - i\epsilon''$.

$$\epsilon' = \frac{C(\text{material})}{C_0} \quad (1)$$

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

This calculation is possible when using the probe we have designed whose geometry is invariant over all measurement conditions. Both the real and the imaginary parts of ϵ^* can have a dipolar and an ionic component [5].

$$\begin{aligned} \epsilon' &= \epsilon'_d + \epsilon'_i \\ \epsilon'' &= \epsilon''_d + \epsilon''_i \end{aligned} \quad (2)$$

The dipolar component arises from rotational diffusion of molecular dipole moments. The frequency dependence of the polar component may be represented by the Cole-Davidson function:

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{(1+i\omega\tau)^\beta} \quad (3)$$

where ϵ_0 and ϵ_∞ are the limiting low and high frequency values of ϵ , τ is a characteristic relaxation time and β is a parameter which measures the distribution in relaxation times. This dipolar term dominates the dielectric signal at high frequencies and in highly viscous media.

The ionic component, ϵ_i^* , often dominates ϵ^* at low frequencies, low viscosities and/or higher temperatures. The presence of mobile ions gives rise to the localized layers of charge near electrodes. Johnson and Cole, while studying formic acid, derived empirical equations for the ionic contribution to ϵ^* [6]. In their equations, these space charge ionic effects have the form

$$\epsilon'_i = C_0 Z_0 \sin \frac{(n\pi)}{2} \omega^{-n} - (n+1) \frac{\sigma}{8.85 \times 10^{-14}} \omega^{-2} \quad (4)$$

where $Z^* = Z_0(i\omega)^{-n}$ is the electrode impedance induced by the ions and n is between 0 and 1 [5-7]. The imaginary part of the ionic component has the form

$$\epsilon''_i = \frac{\sigma}{8.85 \times 10^{-14} \omega} - C_0 Z_0 \cos \frac{(n\pi)}{2} \omega^{-n} - (n+1) \frac{\sigma}{8.85 \times 10^{-14}} \omega^{-2} \quad (5)$$

where σ is the conductivity ($\text{ohm}^{-1} \text{cm}^{-1}$), an intensive variable, in contrast to conductance, $G(\text{ohm}^{-1})$, which is dependent upon cell and sample size. The first term in Eq. 5 is due to the conductance of ions translating through the medium. The second term is due to electrode polarization effects. The second term becomes increasingly significant as the frequency of measurement is decreased.

Reaction Advancement and Effect of Moisture

Both the course of a reaction and the effects of age and moisture on a polymer's cure cycle can be monitored by DDA [2,3]. ϵ'' is sensitive to the ability of dipolar or ionic species to rotate or translate in the polymeric medium. Thus DDA can be used to monitor differences in the concentration of incorporated molecular species as well as reaction rate. Figures 1 and 2 present the dielectric results at a single frequency (500Hz) for 3 samples of the thermosetting polyimide, PMR during polymerization and cross-linking. The samples have been exposed to the identical cure cycle after different pretreatment as follows: Sample 1 was taken directly from a bottle of unreacted PMR in 50% w/w MeOH which had been stored in a freezer. Samples 2 and 3 were removed from this solution and stored, covered but unsealed, in a dessicator at either 0% RH (Sample 2) or 90% RH (Sample 3) for 24 hours. Figure 1 shows the loss curves for the 3 samples during imidization. Sample 1 has an initially very high loss due to the presence of the large amount of solvent MeOH. At about 65°, the boiling point of MeOH, ϵ'' begins to drop as the solvent evaporates. During the 80° hold, one of the acid-amine monomer pairs is preferentially reacting causing the continued drop in the magnitude of ϵ'' . As the temperature is increased at the end of the hold, ϵ'' initially increases, then drops sharply as the effect of the chain-extension reaction overcomes the effect of rising temperature on the viscosity. Sample 2, which was held at 0% RH has partially dried out, losing some of the initial MeOH. The shape of the ϵ'' loss curve remains nearly identical but the magnitude has dropped significantly. Results for the sample exposed to moisture are quite different. The temperature of the initial maximum in ϵ'' is shifted to the initial hold temperature indicating that H₂O has already been exchanged for MeOH in significant amounts. The shallower drop in ϵ'' during the hold monitors the much slower loss of H₂O than MeOH at the hold temperature of 80°. During the post-imidization cross-linking portion of the cure cycle, the effect of volatile incorporation in the resin matrix on the dielectric signal can be observed (Fig. 2). The dry sample had a very small loss throughout the final stages of cure. Both the sample initially high in MeOH and that high in H₂O, however, have a large temperature dependent loss which slowly decays as the resin

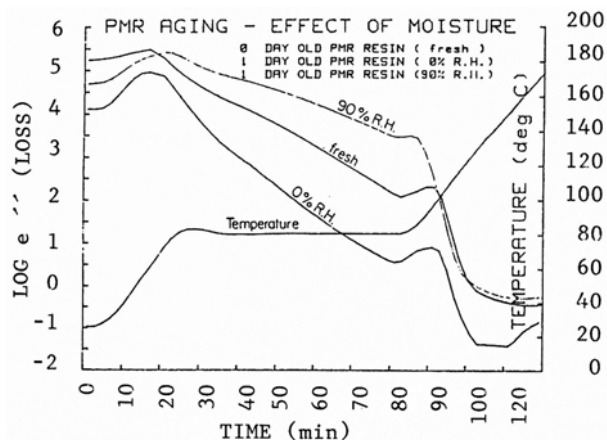


Figure 1. $\text{Log } \epsilon''$ vs. time at 500 Hz for imidizing PMR-15 resin exposed to different storage conditions. The "fresh" sample was run immediately after thawing. The "0% R. H." and "90% R. H." samples were stored at room temperature at the designated relative humidity for 24 hours.

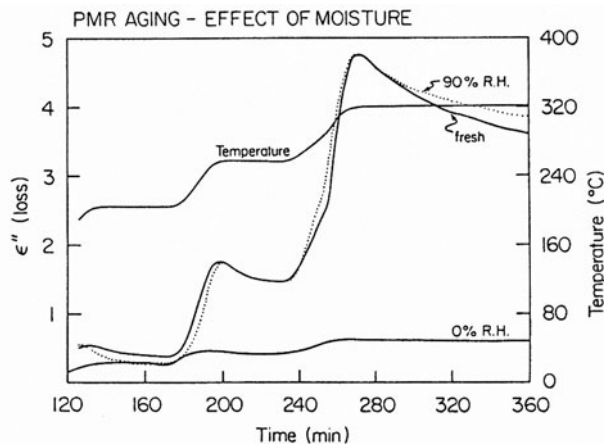


Figure 2. ϵ'' vs. time for cross-linking PMR-15. Sample storage conditions are as for Fig. 5.

cures at each hold. The magnitude of the loss is remarkably similar for samples 1 and 3. A possible explanation for this result is that these two samples represent a condition of maximum solvent complexation (MeOH or H_2O), that it is the volatile impurity which is responsible for the dielectric loss and that the mechanism and ease of motion is sufficiently alike for the two species to give rise to dielectric losses of similar magnitude. More quantitative studies would have to be undertaken to confirm this hypothesis.

Thermoplastic Phase Changes

DDA has been used to monitor phase changes in thermoplastic materials. DSC studies have shown that LaRC-TPI powder is a semi-crystalline material with an initial T_g of 180°C and melt temp of 280° . However, if the material is held at 290° for a period of time, a higher melting crystalline phase slowly forms. These phenomena of softening, melting, and recrystallization

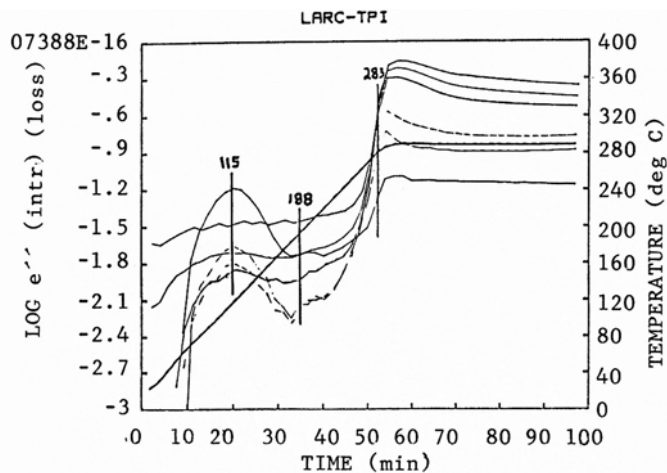


Figure 3. Log ϵ'' vs. time for LaRC-TPI powder during a ramp to and hold at 290°.

can also be observed dielectrically in LaRC-TPI (Fig. 3). The early peak is due to residual solvent being driven out of the resin powder. Just above T_g there is a small, frequency dependent α peak. It is followed by a large sharp increase in ϵ'' as the crystallites melt and the viscosity of the material drops. As the material is held at 290°C, a slow drop in ϵ'' monitors the formation of the higher melting crystal phase.

DSC measurements were made on PEEK during a thermal scan to 400°C and the subsequent cooling curve (Fig. 4). The heating/cooling rate was $\pm 5^\circ\text{C}/\text{min}$. As the temperature increases, a T_g can be observed at 145°C. A broad melting endotherm is observed with an onset at 305° and a midpoint of 340°C. During cooling, a sharp recrystallization of the super-cooled fluid occurs at 290°C, and T_g can be observed in an expanded plot at 145°C. The positions where each of these transitions occur are marked on a DDA plot of $\epsilon'' \cdot \omega$ (Fig. 5). The $\epsilon'' \cdot \omega$ representation of the

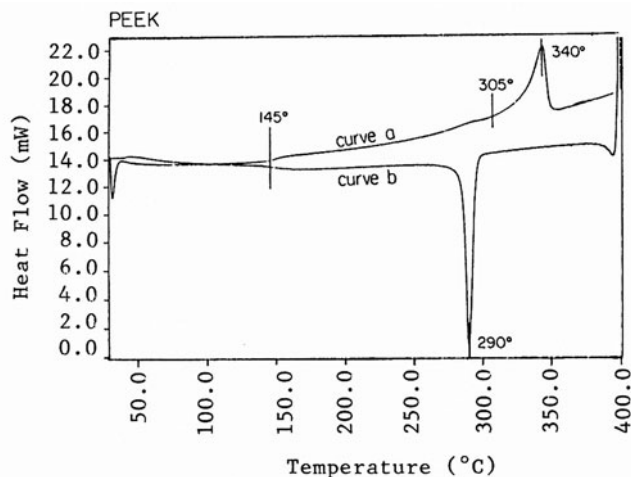


Figure 4. A DSC scan of PEEK during heating to 400° and subsequent cooling. The ramp rate was $\pm 20^\circ\text{C}/\text{min}$. The T_g at 145°C is independent of ramp rate and previous thermal history. A melting endotherm is observed at 345° with an onset at 305° (T_m). Recrystallization occurs from the supercooled fluid at 290°C (T_{cr}).

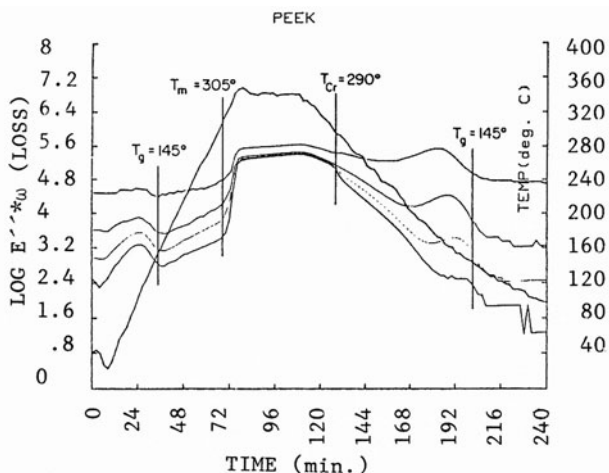


Figure 5. DDA results for PEEK heated to 400°C, held for and re-cooled. T_g , T_m and T_{cr} are labeled in the figure. The low temperature peak is due to solvent/moisture volatilization. Just above T_g , the thermoplastic material wets the sensor obscuring the α -peak. This peak is clearly seen just above T_g in the cooling portion of the curve.

dielectric response allows one to visually observe ionic and dipolar contributions to the dielectric loss. Whenever the curves differ at each frequency, they are dominated by dipole-like phenomena. Overlapping curves indicate translational motion of ions. The low temperature dipole-like peak is due to residual solvent and moisture evolution. Just above T_g the loss increases as the resin coats the probe. As the resin melts the loss increases dramatically. Above the melting point the curves at the lower frequencies converge because ionic translation through the more fluid medium dominates the signal. As the resin cools, recrystallization from the supercooled melt phase occurs at 290°. The recrystallization is shown dielectrically by the drop in the magnitude of the low-frequency loss and by the spreading apart of the curves at different frequencies due to constrained ionic motion in the semi-crystalline material. The frequency dependent dipolar α -peak is observed just above T_g .

In-Situ Viscosity Sensing

From the frequency dependence of the dielectric loss the ionic component can be extracted (see eq. 5). This parameter has been shown to be directly related to viscosity above T_g [8,10]. A special accessory has been constructed for the Rheometrics System 4 Rheometer which allows the simultaneous measurement of rheologic, dielectric and acoustic information.

Figure 6 is a plot of the data from simultaneous viscosity, dielectric and acoustic measurements made on a BF_3 :amine catalyzed TGDDM-DDS resin system. Before the gel point is reached, the ionic mobility parameter and acoustic velocity follow the viscosity. At about 140 min. the viscosity increases dramatically as the resin gels. Beyond this point the acoustic and dielectric signals monitor the buildup in the crosslink density as the reaction continues in the curing resin matrix.

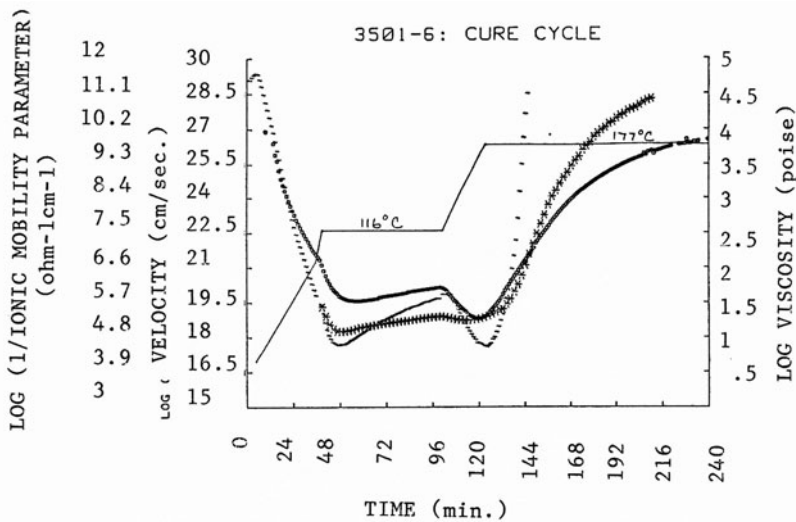


Figure 6. $\log (\text{ionic mobility parameter})^{-1}$, acoustic velocity (*), and \log viscosity (-) vs. time for a BF_3 :amine catalyzed TGDDM-DDS resin.

Variation in Cure Rate Within a Thick Part

Once the dielectric profile for a given resin system has been determined this technique can be used to monitor variation in the rate of cure at different positions within a thick laminate. Figure 7 is a comparison of the dielectric loss, ϵ'' at 250 Hz measured by four dielectric sensors within a 192 ply epoxy/graphite composite. The temperature at each of these positions is also shown. The sensors were placed near the center of a given ply at depths of 0, 32, 64 and 96 plies. Thermocouples measured the temperature adjacent to each dielectric sensor. The experiment was performed in an autoclave on a double-bagged specimen at 100psi. The lag in the advancement of the reaction, i.e., viscosity and degree of cure at a given ply depth is shown by the ϵ'' curves. The lag increases with increasing depth within the laminate and is consistent with time dependence of the temperature at the same depth.

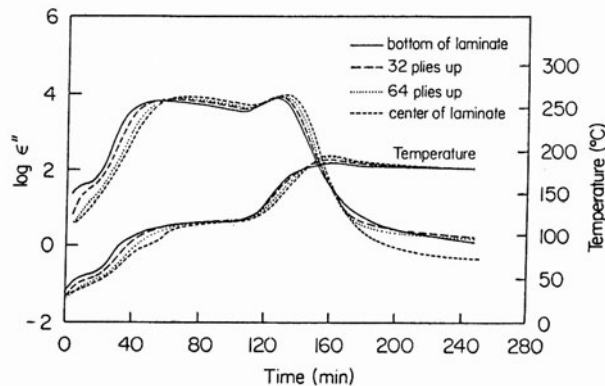


Figure 7. $\log \epsilon''$ (250 Hz) vs. time at increasing depth within a 192 ply catalyzed TGDDM-DDS graphite composite prepreg. Temperatures measured by thermocouples adjacent to each probe are also plotted.

CONCLUSIONS

DDA is an effective in-situ non-destructive method for monitoring reaction advancement in thermosets and phase changes in thermoplastics. The technique is sensitive enough to monitor the slow reactions late in cure and recrystallization during annealing. Effects of moisture and resin history on reaction rate can be observed. From the frequency dependence of the dielectric signal, ionic and dipolar contributions can be determined. It has been found that the ionic mobility parameter is a particularly good monitor of viscosity above T_g . The ability of DDA to monitor variations in the cure rate within a thick part in an autoclave has been demonstrated.

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* Inquiries regarding the Dek Dyne sensor probe and the DDA instrumentation should be directed to D. E. Kranbuehl.

DISCUSSION

From the floor: How would you compare that with the acoustics?

Mr. Kranbuehl: How would I compare it with acoustics? It will be very helpful to have a variety of sensors, particularly when looking at high-performance, difficult-to-process materials. The various sensors will tend to be most sensitive to different aspects of the reaction.

It's important to know that in acoustics, you make measurements at a high frequency. Just like in dielectrics, it is giving you a probe of an effective viscosity over smaller dimensions than the actual bulk low-frequency limit of viscosity which affects how a resin fills a tool or flows around the cloth in a composite prepreg.

Acoustics does have problems when bubbles are present. However, every sensing technique has its own problems. I look forward to acoustics being an effective aid, which compliments dielectrics.

Mr. Jeff Chambers with DuPont: Do you envision using this kind of technique for actual measurement on a product which would go out and be a useful part? Looks like you have sensors imbedded in the middle of the composite.

Mr. Kranbuehl: Without question on a product. We are in the middle of working with people in production in terms of automating a processing tool so that you can reproducibly turn out parts particularly when you are dealing with \$50-to-\$300-a-pound prepreg material.

I see frequency dependent dielectric measurements as a valuable aid for people who are developing new resins so that you can determine the processing properties, develop an effective processing cycle and understand the resin's processing properties much faster than the time it now takes to bring a new formulation to a reliable processable resin.

But the answer to your second question is, it is relatively easy to put a sensor in a position where it will be cut out of the final part or even in a dummy part among many parts in the autoclave. Sensors can also be built into the tool.

Mr. Bonner Staff, Lockheed, Georgia: As you know, we are engaged in some similar kinds of work. I'll say "yes" to your response to the gentleman in terms of production monitoring. This is a direction that we are in as well.

Would you comment on mobile charge and the source of that free mobile ion? There's some debate as to whether or not some of these materials naturally have a free mobile ion or whether this is a contaminant of some sort.

Mr. Kranbuehl: I don't know how to use the word "contaminant" in an industrial process. When you produce something in large scale and you don't go through extensive efforts to purify it, like distilling water--and there's degrees of how clean you get water--you pick up ions. Ions are ubiquitous. They're on glass. They are all around us. Thus resins, when processed in bulk, will pick up more ions than resins made by synthetic chemists in a research laboratory.

There are also ions in various resins, such as polyimides, which are intrinsic to the material. Whenever you have

hydrogen bonding, alcohols and so forth, you are going to have protons, and these ion-charged species are an integral part of the material.

Mr. Staff: Do you consider your uninsulated electrodes the source of these ions?

Mr. Kranbuehl: No! An interesting point is that the number of ions is quite uniform. The changing flow properties of the material as it polymerizes causes far greater variation.

I should add that we are involved in research on understanding in detail the mechanisms of the ionic conductivity in these various resins.

From the Floor: Are you measuring the difference in dielectric properties between the crystalline phase and amorphous phase in the (thermoplastics) and-

Mr. Kranbuehl: Yes. This sensing technique is going to be a very valuable tool in addressing processing questions for high-performance thermoplastics as well as thermosets.