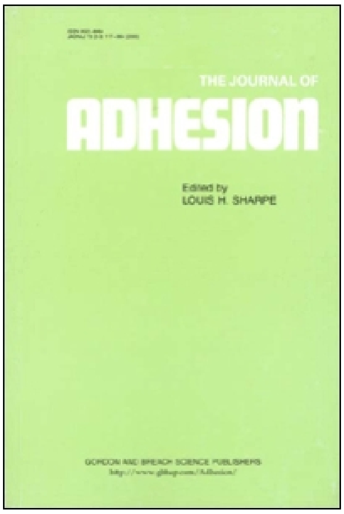

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Dielectric Monitoring of the Bonding Process

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The changes in the dielectric properties of a curing thermoset adhesive can be correlated with the chemical and rheological changes that occur during the cure. The progress towards the use of these real time events to control the bonding process is discussed. The primary mathematical relationships are described, the influence of chemical structure is discussed, monitoring under shop conditions is demonstrated and a correlation between the dielectric signal, heat of reaction and wetting angle is developed for a specific adhesive.

INTRODUCTION

Dynamic dielectric analysis (DDA) measurements have been shown to reflect the chemical and rheological changes which occur during the cure of a thermoset resin.[1–6] Our studies have shown that the method is of great value in the development and control of processes involving fiber reinforced composites[7–9] and adhesive bonding.[10] It is the purpose of this paper to discuss progress towards the goal of applying control to the bonding process by means of a closed loop, computerized system based on dielectric signals.

Dielectric and physical measurements are termed analogous systems since they are governed by similar mathematical relations.[11] This permits the construction of a force-voltage analogy as shown in Table I. However, we have observed that, depending on the dipoles within a particular polymer structure, the dielectric and mechanical response may not be completely analogous. Thus the real time utility of the method depends on developing clear correlations between the dielectric signal and the significant chemical and physical events of the cure.

Presented at the Annual Meeting of The Adhesion Society, Savannah, GA, U.S.A., February 10–13, 1980.

TABLE I

Conversions for force-voltage analogy

Mechanical System	Electrical System
Force	Voltage
Velocity	Current
Displacement	Charge
Mass	Inductance
Damping Coefficient	Resistance
Compliance	Capacitance
Mechanical Loss	Loss Tangent

As an example, consider the dielectric response curve in Figure 1. The data was generated on a typical 177°C (350°F) epoxy resin system using Tetrahedron's Audrey Dielectrometer. In this figure capacitance and dissipation have been plotted as a function of time for the cure cycle indicated. The dissipation curve can be interpreted in terms of the chemorheological changes. However, the exact location of the lowest viscosity and the resin gel point must be determined by other rheological methods. The left hand peak results from the softening of the prepreg matrix as the temperature increases. The right hand peak is associated with the chemistry of the cure and hardening of the resin. Between the two peaks is a region where the resin viscosity is low. Understanding this region is important in the processing of the material. In the cure of an adhesive, this is where wetting of the substrates occur. When the

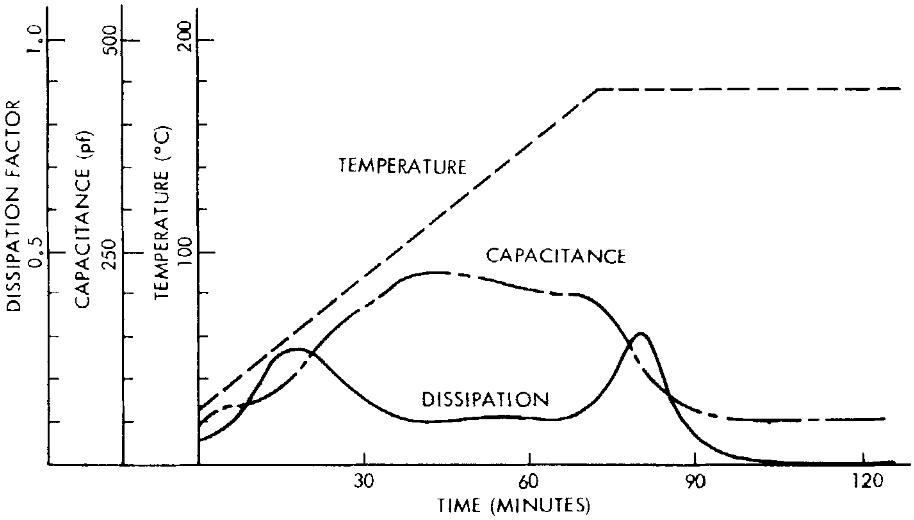

FIGURE 1 Dielectric response of a 350°F epoxy resin.

dissipation factor no longer changes beyond the second peak, no further cure is occurring at that temperature.

The first part of this article deals with the techniques used to monitor the bonding process and how they interrelate. After a discussion on the influence of chemical structure and B-stage, the use of this technology to monitor actual part production will be described. Finally, correlations between dielectric signals and physical measurements such as wetting angle and differential scanning calorimetry (rate of cure) will be discussed for a typical 177°C (350°F) curing adhesive.

MONITORING TECHNOLOGY

Three methods are available for monitoring thermoset resin cures. These methods vary in both the complexity of the equipment required and the sophistication of the data obtained. One method, iongraphing, measures conductivity changes as they occur in a resin system during cure. The Audrey and phasemeter techniques measure dipole mobility in a resin system as reflected by changes in the dielectric properties. Prior work on epoxy resin systems indicates that these dielectric changes can be related to physiochemical changes occurring during the cure of a selected material. A comparison of the three methods on the same adhesive is shown in Figure 2.[12] The material was an elastomer-modified 177°C (350°F) curing epoxy adhesive heated to the cure temperature at a rate of 2°C per minute.

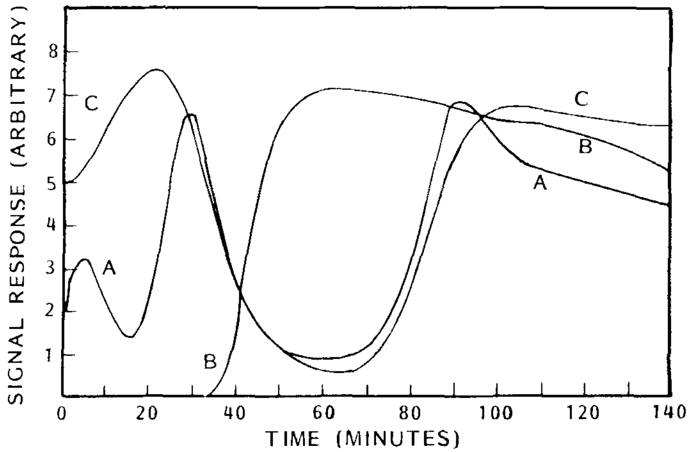

FIGURE 2 Comparison of dielectric monitoring traces. A) Audrey dielectrometer, B) Iongraphing, C) Phasemeter.

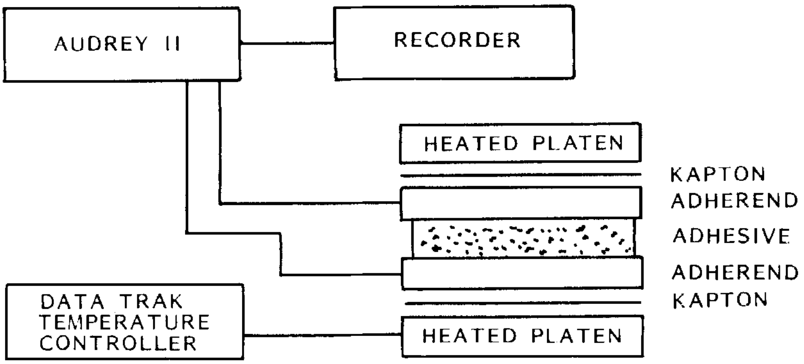

FIGURE 3 Dielectrometer block diagram.

The Audrey technique appears to be the most chemorheologically definitive of the three methods. Because this is a commercial instrument, the circuitry is not detailed herein, however, Figure 3 shows a block diagram of the component relationships. This is an AC measurement at an applied voltage of one volt, and requires a preselected frequency between 100 and 1000 Hz. In Figure 2, curve A, three peaks are evident. It has been speculated that the first peak, which occurs at 44°C during heating, is associated with a pseudocrystalline change in the nitrile elastomer component of the formulation.[12] Whereas the method has an excellent potential for chemorheological definition, there are inherent drawbacks. The low operating voltage dictates a low signal-to-noise ratio and this makes the method difficult to use in a production environment. The instrument also has an internal ground system. Since a part must be isolated from true ground, this technique is not amenable to production processes such as autoclaving. In Figure 3, the layers of Kapton film provide electrical isolation from the grounded platens.

Iongraphing measures voltage changes that are directly related to conductivity changes during adhesive cure. The necessary equipment is simple. A DC power supply, a reference resistor, adhesive between electrodes (adherends), a recorder (voltmeter) and a programmed heating source are all that is needed. The related circuit is shown in Figure 4.

This system is obviously inexpensive, but as evident from Figure 2, curve B lacks definition in the process critical (low viscosity) region. Decision points such as where to apply pressure are thus difficult to define. Because this is a DC measurement, polarization effects can make the results difficult to interpret in terms of chemical reactions and physical response.

Monitoring by measurement of the changes in phase angle and vector voltage offers a reasonable compromise between the two aforementioned methods. It gives better definition than iongraphing and can be used over a

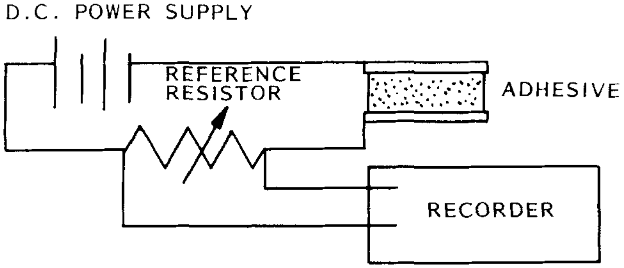

FIGURE 4 Iongraphing schematic.

wide range of frequencies and voltages. The system can be constructed from off-the-shelf components. As shown in Figure 5, an oscillator impresses an AC signal through a reference resistor and an adhesive sample to ground. The higher voltage capability, as compared to the Audrey system, results in a higher signal to noise ratio. This approach also offers a common ground for both the monitoring system and processing equipment. In Figure 2C the phase angle trace is less definitive than the Audrey data, but appears adequate in the process critical region where both signals pass through a minimum.

Monitoring probe technology is relatively simple. We have demonstrated that the faying surfaces can be used as the electrodes or a simple foil probe can be placed directly in the bond line. When using the faying surfaces, they must be isolated from electrically conductive surfaces such as press platens. This is illustrated in Figure 6. In the case of an internal probe, a piece of thin aluminum foil is placed directly in the bondline as shown in Figure 7. Each of the faying surfaces acts as another electrode and the probe remains permanently imbedded in the bondline. Electrical insulation of the part is not required. Results indicate that the imbedded probe has a minimal effect on the lap shear strength of the bond.

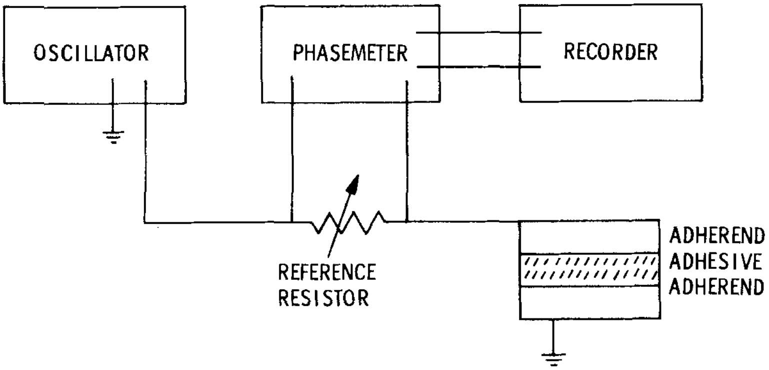

FIGURE 5 Phasemeter schematic.

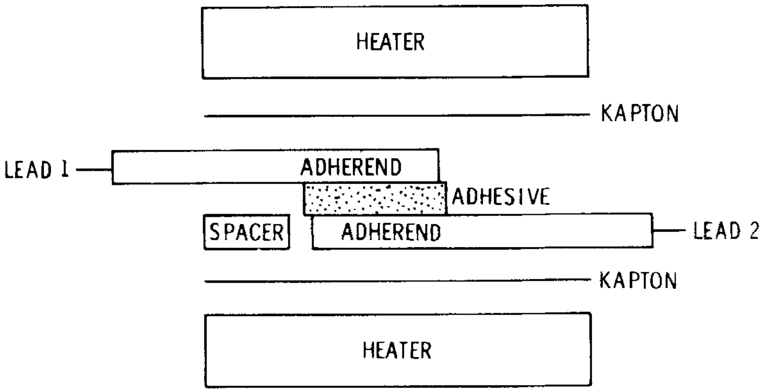

FIGURE 6 Direct probing configuration.

An interesting aspect of bond monitoring occurs during the fabrication of honeycomb core panels. A variety of measurements can be made depending on the bondline(s) of interest as illustrated in Figure 8. In Figure 8A the signal from lead 1 (attached to conductive core) follows the progress of the cure in the lower bondline while the signal from lead 2 is related to the cure progress in both bondlines. In Figure 8B, where the core is the ground plane, leads 1 and 2 follow the cure in the lower and upper bondlines, respectively. Figure 8C illustrates how a foil probe may be combined with the faying surfaces. The signal obtained from an inserted probe gives specific information at one location while the overall bonding process is simultaneously measured as in Figure 8B.

The phasemeter and Audrey data can be related mathematically. Agreement between the two methods, indicated in Figure 9, is quite good. This is a plot of the magnitude of tan ϕ_s, the phase angle across a sample, as a function of time and temperature for a preselected cure cycle. The dissipation factors were calculated from separate Audrey and phasemeter monitoring experiments. The sections of both curves (shaded symbols) between singularities reflect phase angles greater than 90° and hence have negative tangent values. Since negative values of tan ϕ_s have no physical significance, it is

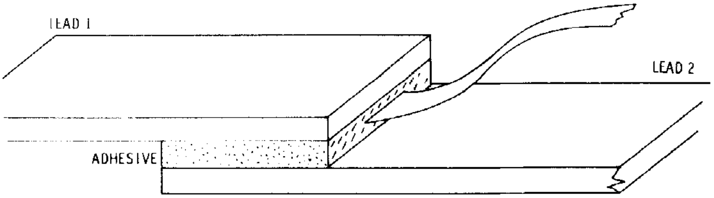

FIGURE 7 Foil probe in bondline.

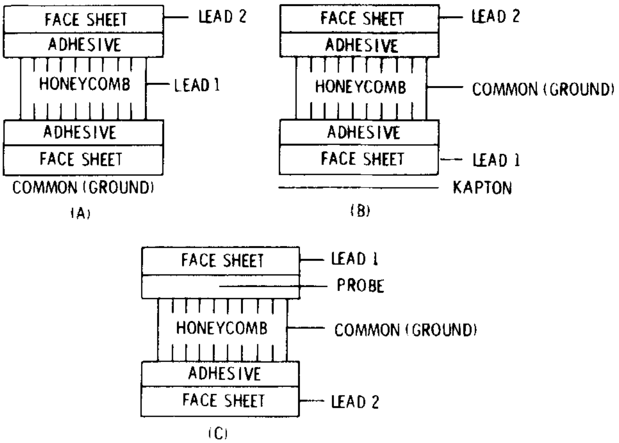

FIGURE 8 Honeycomb monitoring configurations.

suspected that the simplistic circuit model requires refinement. It should also be noted that the agreement is dependent upon selection of the reference resistances. It was experimentally determined that a reference resistance of 100 kΩ for the Audrey and 10 MΩ for the phasemeter system give comparable responses. A more thorough analysis of the two circuits is now in progress so that a better understanding of this experimental observation may be gained.

Based on results from both contractual and independent developmental efforts, it has been observed that a high degree of signal reproducibility is possible in dielectric monitoring of the adhesive bonding process. Work remains to be done on how the probe influences the mechanical properties of the bond. However, preliminary results under both ambient conditions and after various environmental exposures indicate the effects of the foil probes are minimal. It would thus appear that once a correlation is developed between the dielectric signals and the chemorheological properties of a particular adhesive, automation can be devised whereby dielectric properties can be used to control the time-temperature-pressure relationships of the bonding process.

INFLUENCE OF CHEMICAL STRUCTURE

The chemical structure of the materials being monitored have a definite influence on the shape of the dielectric measurement curves. Not only do the curves differ as the chemical structure of the resin changes, but less subtle changes such as misformulations or the degree of B-staging can also be detected. B-staging refers to the prereaction of the resin system during the adhesive manufacture.

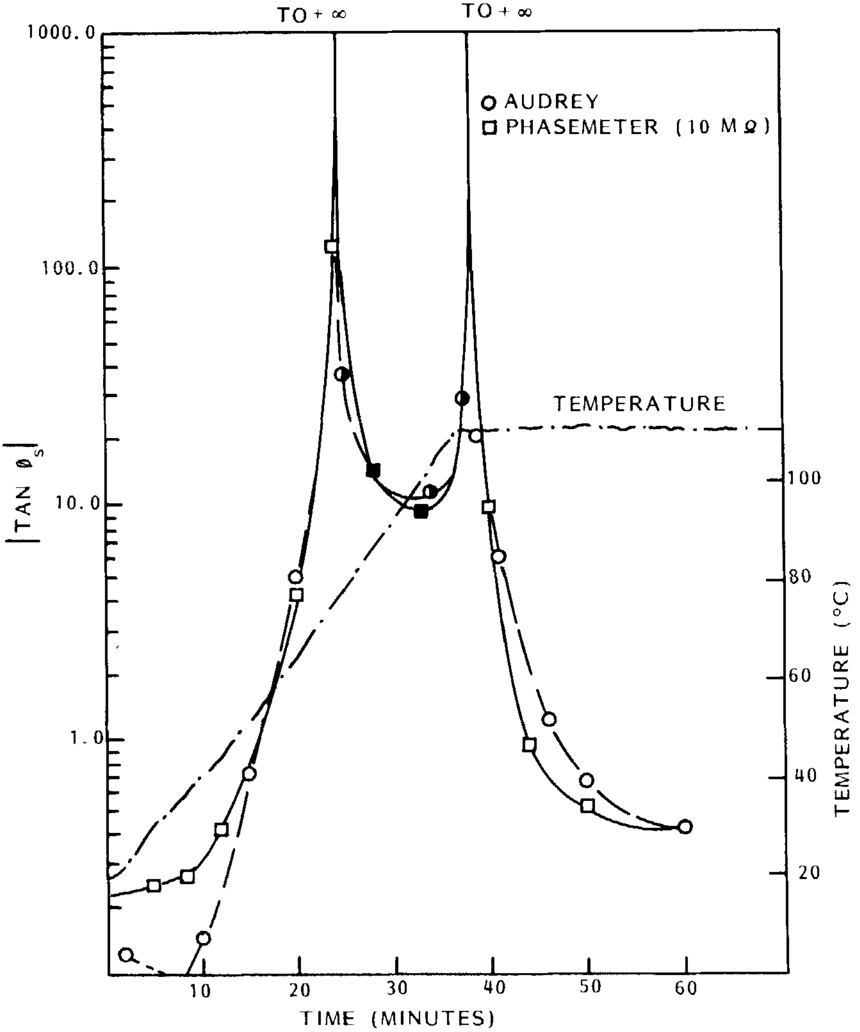

FIGURE 9 Comparison of absolute sample dissipation factors calculated from Audrey and phasemeter measurements.

Shown in Figure 10 are the dielectric measurements for an acetylene terminated polyimide (ATI)[13] developed by Hughes Aircraft Corporation under contract to the Air Force.[14] It is currently marketed by Gulf Chemical under the trade name Thermid 600. When heated at a rate approximating that of the epoxy formulation (Figure 2), the Audrey dissipation factor data is quite different. The processing window, which appears in the neighborhood of 207°C is much narrower than that displayed by the epoxy. The lower

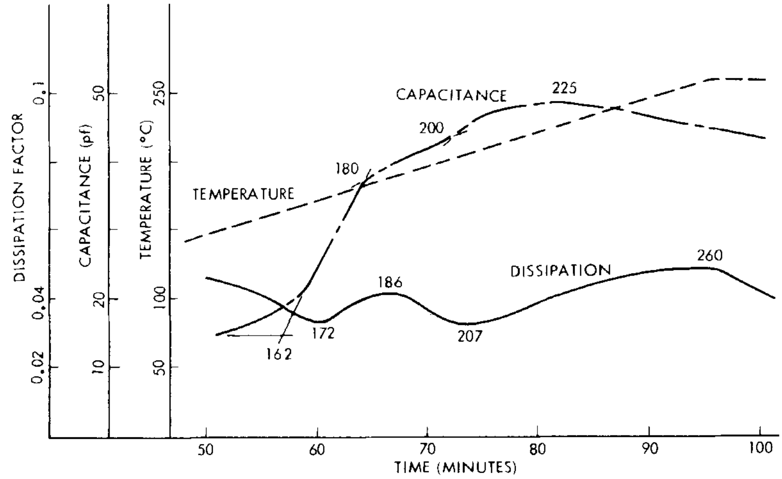

FIGURE 10 Dielectric curves for acetylene terminated polyimide.

magnitude of the dissipation peaks (note the difference in scale magnitudes) also suggests less reduction in viscosity in this region, a sign of more difficult processing. Indeed, Thermid 600 does exhibit much less flow than the epoxy formulation.

Formulation variations produce more subtle changes in the dielectric response. Shown in Figure 11 are the results obtained when the resin curing agent ratio of an epoxy formulation was purposely varied. A decrease in the curing agent concentration shifts the minimum phase angle to a longer time. This is not unexpected since a reduction in the amount of curing agent should result in a slower cure. Although changes in curing agent concentration can be detected by dielectric analysis, the procedure is probably not sufficiently definitive for formulative quality assurance. High pressure liquid chromatography is currently considered the best method for this purpose.[15]

The level of molecular mobility detected by DDA after cure depends on the selection of a cure temperature relative to the ultimate T_g.[16] The 177°C (350°F) resin system data of Figure 1 is the result of curing CIBA-Giegy MY-720 with diaminodiphenylsulfone. At the completion of cure, the resin T_g exceeds the cure temperature, segmental dipole motion ceases and the observed dissipation factor is very small. Figure 12 illustrates the cure of an epoxy novolac with dicyandiamide. Since cure temperature used is above the T_g capability of the system, molecular segmental motions are possible and the dissipation factor remains high in the latter stages of the cure.

The degree of B-staging or prereaction prior to cure can also be detected by DDA. Figure 13 illustrates the effects of aging at 80°C on the 177°C (350°C) resin matrix prior to submitting the material to the same cure cycle used in

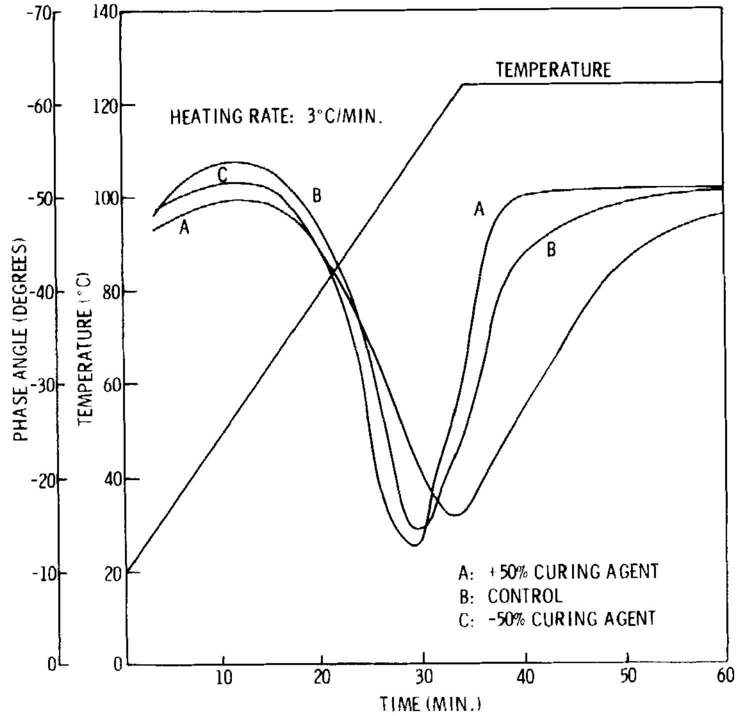

FIGURE 11 Effects of chemical formulation on dielectric response.

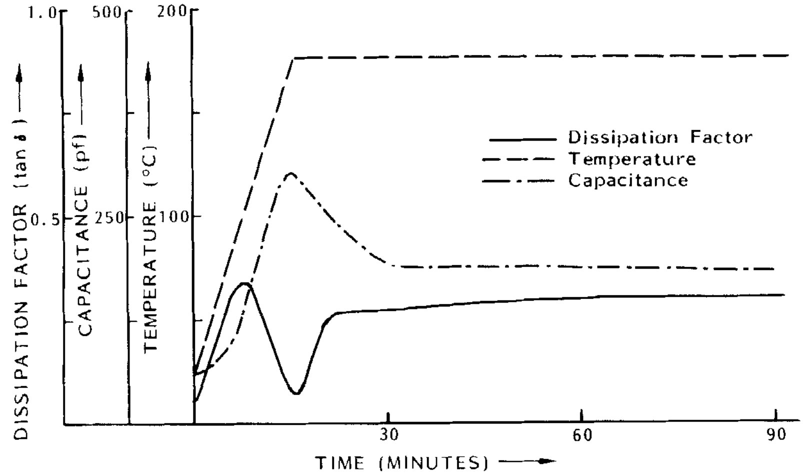

FIGURE 12 Dielectric analysis of a dicyandiamide/epoxy Novolac cure.

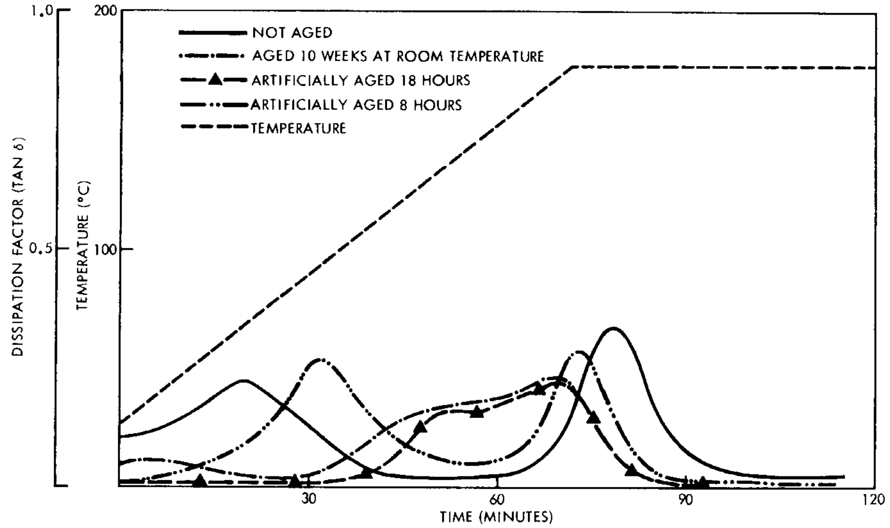

FIGURE 13 Effects of aging on dielectric response.

Figure 1. Aging raises the softening temperature of the resin so that the softening peak moves to the right. In addition, aging consumes chemically reactive groups, thereby narrowing the processing window. Note that as the aging continues, the two peaks lose definition. This indicates, for this degree of aging, that the heating rate is too slow to permit sufficient softening of the resin and poor wetting would result in a bonding process. A faster heating rate is therefore required. This is an important consideration in developing real time, automated process controls.

PRODUCTION MONITORING

Dielectric monitoring has been successfully demonstrated in a production environment. This was done as part of an Air Force program called PABST (Primary Adhesive Bonded Structures Technology), wherein a 53-ft section of a YC-15 fuselage was stiffened entirely by adhesive bonding.[17] A picture of the monitored part is shown in Figure 14. It measured approximately 10′ × 30′. Bonding was carried out in an autoclave. Because of the part size, there was concern that the cure of the adhesive was non-uniform and weak points in the structure would result.

The probes used to generate the dielectric signals were placed directly adjacent to parts being bonded. The probe assembly is shown in Figure 15. A layer of adhesive was placed on either side of an aluminum foil probe so that it

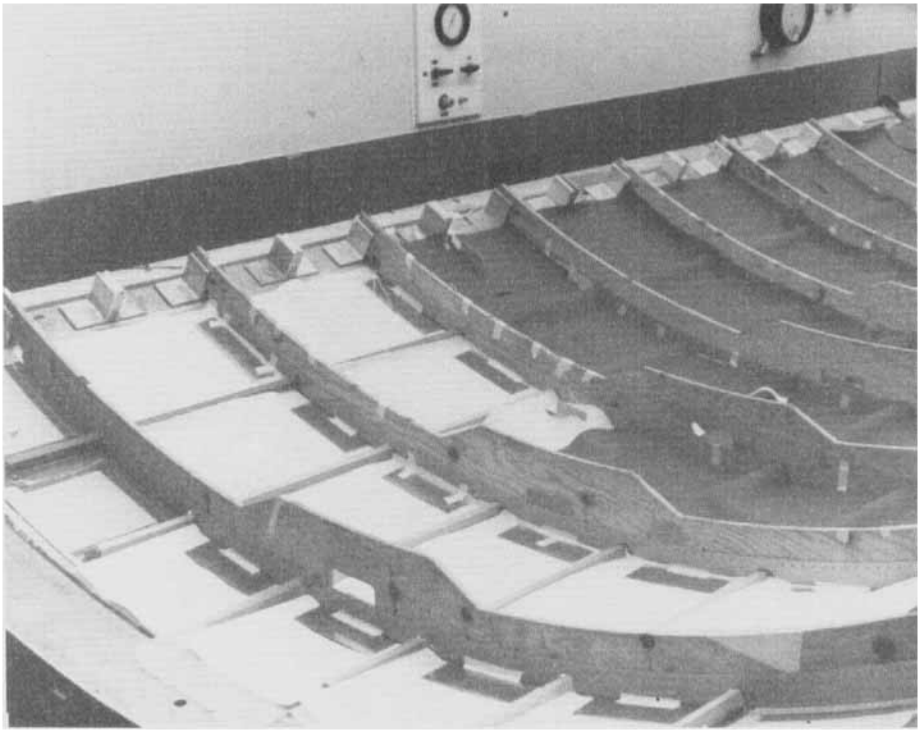

FIGURE 14 Fuselage section and monitoring assembly locations.

would not short to either of the faying surfaces. The upper faying surface was a small section of rib, while the lower one was an aluminum sheet resembling the skin of the fuselage. Electrical contact was made by a piece of copper-coated Kapton film folded over the probe and connected to a monitoring lead wire. This was taped to the sheet to prevent slippage when pressure was applied to the bonding assembly. After completion of the cure, the monitoring assembly was easily removed. Later in the program, confidence in the method grew to the point where a monitoring foil probe was placed directly in a bondline.

The dielectric monitoring curves from two probes in a typical production run are shown in Figure 16. The phase angle minima occur at different temperatures indicating that the adhesive was curing at different rates in different sections of the part. These differences are probably too small to cause bond strength differences at the two locations and it was subsequently demonstrated by Douglas[18] that the fuselage section was a highly useful structure. Undoubtedly, large differences in the dielectric monitoring traces can be used as an indication of residual bondline stresses. However, a quantitative interpretation has yet to be accomplished.

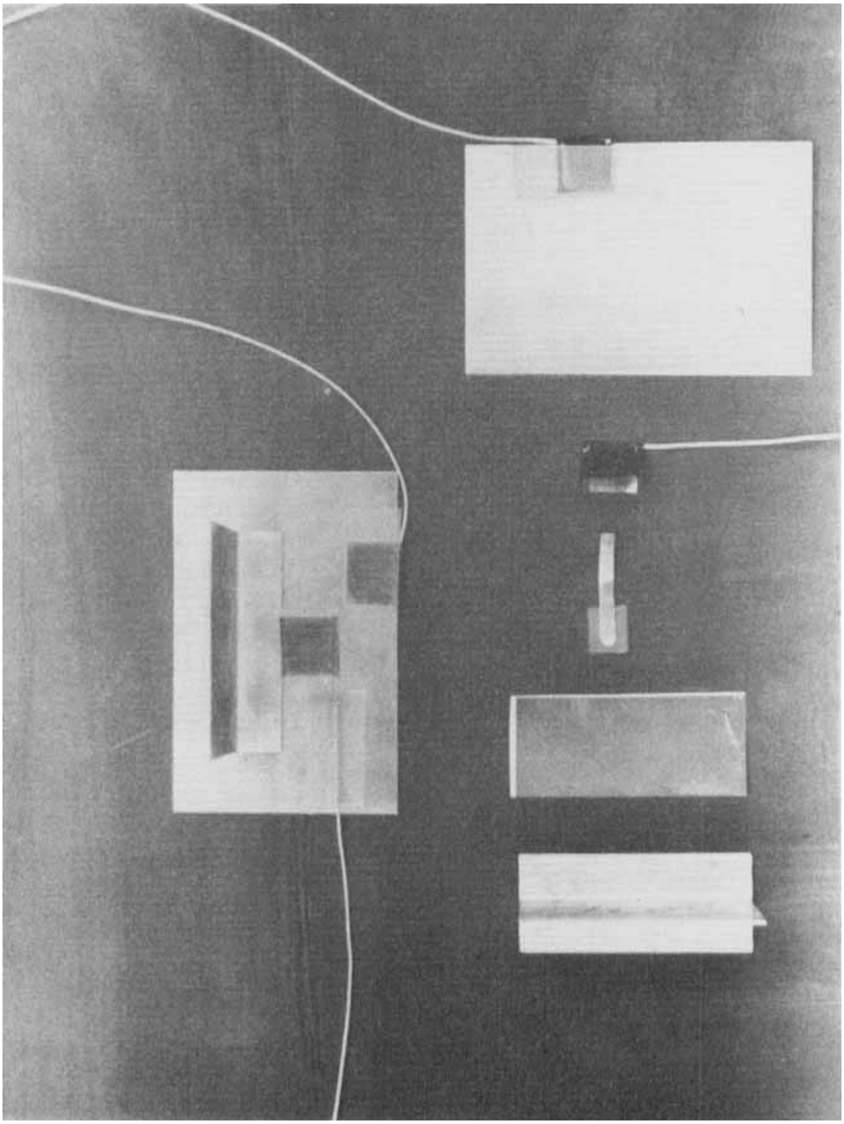

FIGURE 15 Components of a monitoring assembly.

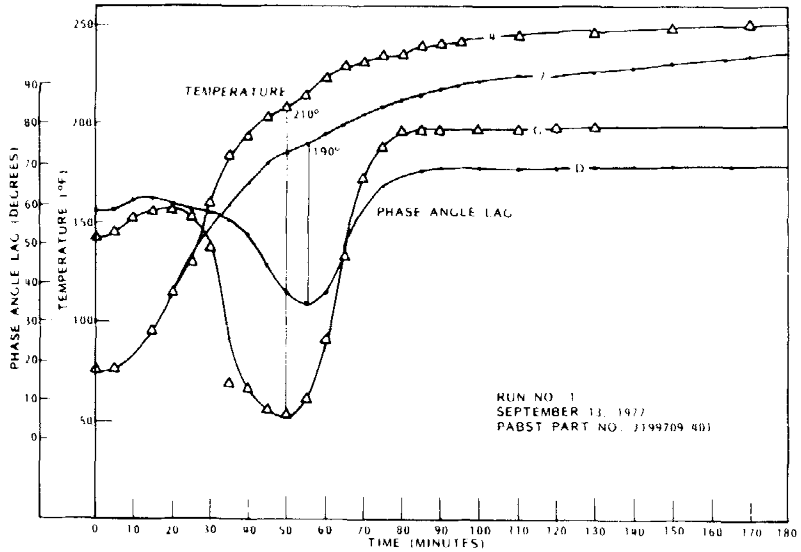

FIGURE 16 Dielectric monitoring curves for autoclave-cured fuselage section.

Figure 17 compares wetting angle and heat evolved during cure with dielectric dissipation (Audrey) for the 177°C (350°F) curing adhesive referred to in Figure 2. It shows that the minimum wetting angle is limited by the onset of the curing reaction. Thus heating rate can influence the degree of wetting during the bonding process. The minimum wetting angle and the onset of the curing reaction occur in a region where a minimum dissipation factor is

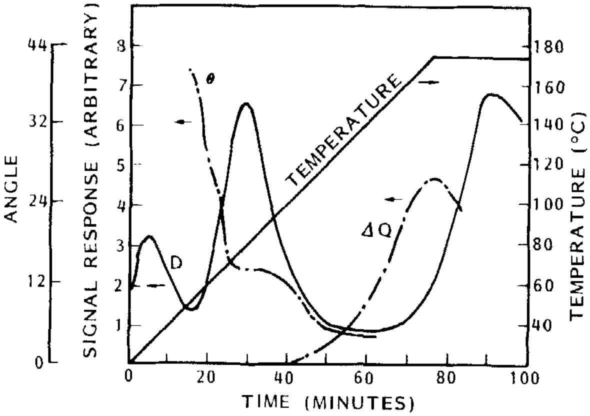

FIGURE 17 Simultaneous measurement of wetting angle (θ), heat evolved during cure (ΔQ) and dissipation factor (D).

observed. Thus the shape of the DDA curve can be a useful indicator of the degree of wetting during a bonding operation.

Overall, the results of our investigation to date indicate that dielectric analysis can be used to monitor the real time physical and chemical changes in a resin as curing progresses. Studies are now being extended to correlate dielectric measurements with actual viscosity changes and the chemical kinetics of the cure. As this knowledge develops, it is becoming increasingly apparent that the real time events of the cure, detected by dielectric analysis, can be used to automatically control a bonding operation in either a press or an autoclave. This technique, when combined with rigorous chemical and B-stage control of the starting adhesive, would be a highly reliable method of assuring high quality bonded structures.

Acknowledgements

The breadth of the program discussed in this review could not have been accomplished without the help of others. We would particularly like to thank Deborah K. Hadad and John S. Fritzen of LMSC for their many contributions which have led to a better understanding of dielectric analysis. We are also grateful to the late E. A. Arvay and H. S. Schwartz of AFML for their council and for arranging funding for portions of our studies.

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