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CURE MONITORING TECHNIQUES FOR ADHESIVE BONDING PROCESSES

LOCKHEED MISSILES & SPACE COMPANY, INC.
P. O. BOX 504
SUNNYVALE, CALIFORNIA 94088

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WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

NOTICE

This technical report has been reviewed and is approved for publication.

Edward A. Arvay

EDWARD A. ARVAY

Project Engineer

FOR THE COMMANDER

T J Reinhart

T.J. REINHART, Chief
Composite and Fibrous Materials Branch
Nonmetallic Materials Division

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Dielectric monitoring was successfully applied to the adhesive bonding process for structural aerospace adhesives. Of the three methods investigated, the one best suited for production applications was demonstrated for flat adherends of various substrates and aluminum honeycomb panels. A monitoring technique which uses a foil probe embedded in the bondline permits multipoint cure monitoring in a single bondline. Effects of the probe on bondline strength were determined. Lap shear specimens bonded with B. F. Goodrich's PL-729 and

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20. ABSTRACT (Continued)

American Cyanamid's FM-73 were exposed to four moisture environments and tested at room temperature.

FOREWORD

This technical report summarizes the work conducted by the Manufacturing Research Laboratory of Lockheed Missiles & Space Company, Inc., Sunnyvale, California 94086 under USAF Contract No. F33615-76-C-5170. This contract was initiated under Project 7340, "Nonmetallics and Composites Materials" Task 734002, "Structural Adhesives". The work was administered under the direction of the Nonmetallics Materials Division, Air Force Materials Laboratory, with Mr. E. A. Arvay (AFML/MBC) as Project Engineer.

The principal investigator was C. A. May. The laboratory work was accomplished by A. Wereta, Jr., W. J. Warren and J. S. Fritzen who were responsible for the development of the techniques used. This project was conducted during the period 15 April 1976 to 17 January 1977 and was submitted by the authors on 1 March 1977.

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INTRODUCTION

"...When, after cleaning, the boundary layer on a metal is stronger than the adhesive—which condition is usually satisfied when the adhesive is an organic polymer—then rupture occurs in the polymer film, and breaking stress is determined to a large degree by the properties of this film; in brief, the adhint* is of the proper type...." In this quotation by J. J. Bikerman(1) is the unexpressed root of the problem addressed herein. A proper adhesive joint results when the polymer is properly (completely) cured and the substrate has been properly wetted, a prerequisite to a strong boundary layer. The latter phenomenon, wetting, is time dependent and thus is governed by the surface condition of the substrate and the chemical structure of the adhesive, its viscosity and its temperature. Assuming a properly cleaned substrate, reproducible adhesive bonding thus becomes time/temperature dependent—the proper time at the proper temperature for optimum wetting and sufficient time at the cure temperature to ensure a totally crosslinked, stable, consistent polymer film. Thorough attention to these factors results in optimum mechanical and environmental resistance properties of the bond.

Current practice in adhesive bond fabrication is to follow a predetermined cure cycle and to assume that a good bond will result when this practice is followed to the letter. There are, however, obvious disadvantages to this approach. Depending on the thermal history of the product during processing and storage the resin and curing agent have reacted or B-staged. The extent of the B-stage may influence bond properties. For instance, if the components

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*A word used to describe the entire adhesive joint consisting of adherend—adhesive—adherend.

have reacted too far the flow may not be sufficient to properly wet the substrate. In addition, improper formulation may alter the curing characteristics again leading to improper bond formation. Finally, part temperatures, because of size, caul plates, etc., may lag behind the scheduled autoclave or press temperatures causing deviations from the proper cure cycle. These lower temperatures can result in poor wetting of the substrate, undercure of the adhesive and consequently unsatisfactory bond performance. The need for better process controls are thus indicated to assure the fabricator of a highly reproducible process resulting in optimized joint strength and durability.

The main purpose of this investigation was to develop an instrumental monitoring technique that would indicate the formation of an optimum bond on a laboratory scale and have an indicated utility in production processes. The program was highly successful. With little additional effort, the techniques can be used for in-plant process demonstration purposes as of this writing.

Technical developments at LMSC(2-4) and other literature references(5-11) clearly indicate that the rheological properties of curing thermoset resins can be related to changes in the dielectric properties. Further, Arvay and Centers demonstrated the method could be used to monitor the curing of an adhesive and that additional studies were warranted.

During the course of this study, three methods of measurement were considered: (1) "iongraphing" or electrical resistivity determinations, (2) a commercial dielectrometer (Audrey II) which measures capacitance and dissipation factor, and (3) direct measurement of phase angle shift and vector voltage using commercially available components. The merits and drawbacks of each method are considered herein. Bond strength data, wetting angle measurements and differential scanning calorimetry were used to develop supporting evidence. In the final analysis, a simple metal foil probe, inserted directly in the bondline, may well prove to be the key to successful application of dynamic dielectric analysis for monitoring the adhesive bonding process during the manufacture of bonded structures.

Section II

EXPERIMENTAL MATERIALS AND PROCEDURES

II.1 Adhesives

There are a large number of structural adhesives commercially available to the aerospace industry which encompass a wide range of property characteristics and processing requirements. The two materials used for this program are commercially available and were selected because of their importance in the PABST Program (Primary Aircraft Bonding Structures Technology). One adhesive is representative of the 121°C (250°F) service products, the other represents the 177°C (350°F) service class.

FM-73, a product of American Cyanamid Company*, has a nominal operating temperature range of 121°C (250°F). It is an epoxy based film adhesive, supported on a Dacron matte scrim and was designed primarily for metal-to-metal bonding. The recommended primer is BR-127 which is corrosion inhibiting. According to the manufacturer's literature, FM-73 may be cured over a wide range of temperatures, from 93°C to 177°C (200°F to 350°F).

The second material used was PL-729, a product of B. F. Goodrich** which is the 177°C (350°F) service product. It is a nylon tricot scrim supported, epoxy based, film adhesive designed for metal-to-metal bonding and is used with a specifically formulated primer designated as PL-728. This adhesive is normally cured at 177°C (350°F) for 60 minutes.

It should be noted that adhesive formulations are complex. The additives included in these formulations are elastomers, thixotropes, and carriers, in

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*Bloomingdale Aerospace Products, Havre de Grace, MD 21078
**B. F. Goodrich Adhesive Products, Akron, Ohio 44318

addition to expected combinations of epoxy resins, accelerators and curing agents. This is mentioned because the effect of additives on some of the physical measurements made, herein, can be readily observed. Metal powder filled adhesives were avoided because of possible influences on the electrical measurements.

II.2 Adherends

One objective of this program was to examine the effect of the nature of various substrates (adherends) on the monitoring procedures. Adherends studied in this program were aluminum sheet, aluminum honeycomb, titanium sheet, graphite/epoxy composite, and boron/epoxy composite. The aluminum alloy was bare 2024-T3. The titanium alloy was 6Al-4V. The majority of the work accomplished on the program involved the 2024-T3 alloy which is probably the best understood of these substrates and also minimized the cost of materials. The nominal thickness of all metals was 1.51 mm (0.0625 inches). One 12.5 mm (0.5 inch) thick honeycomb core with one quarter inch core size was used. Test coupons of graphite/epoxy 2.03 mm (0.080" thick) and boron/epoxy .508 mm (.020 inches thick) were fashioned from laboratory produced flat composite panels.

Aluminum adherends and honeycomb core were cleaned and etched following the FPL procedure outlined in the Appendix. Adherends were air dried at room temperature for one hour before the appropriate primers were wiped on with a dampened cloth (single pass). Primed surfaces were air dried for a minimum of one hour but never more than three days before applying adhesive.

Titanium adherends were cleaned and etched according to the procedure outlined in the Appendix. Both the method of primer application and the drying schedule were the same as those used for aluminum adherends.

Graphite/epoxy and boron/epoxy composite adherends were simply wiped clean with MEK and air dried for several minutes before lay-up.

II.3 Dielectric Methods

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, "Ion graphing", simply measures the conductivity changes occurring in the resin system during cure. The other two methods, Audrey* and Phasemeter, measure dipole mobility in the resin system as detected by changes in its dielectric properties. Prior work on epoxy resin systems indicates that these dielectric changes can be related to physiochemical changes occurring during the cure of the selected material. The three methods are described in the sections which follow.

II.3.a Iongraphing

Iongraphing measures voltage changes, which are directly related to conductivity changes, during adhesive cure. All that is required for this monitoring method are a DC power supply, a reference resistor, adhesive between electrodes (adherends), a recorder (voltmeter) and a programmed heating source. The related circuit is shown in Figure 1.

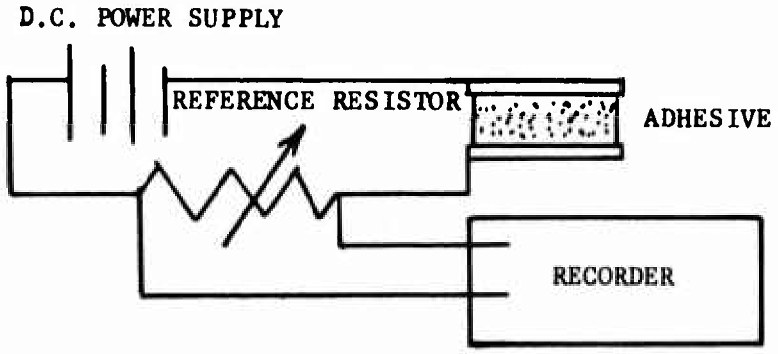

Figure 1. Iongraphing Schematic

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*Audrey II Dielectrometer, Tetrahedron Associates, Inc., San Diego, CA 92111

This method was applied to a lap shear specimen consisting of PL-729 and aluminum adherends. A programmed hot plate was used to cure the adhesive with an approximate heating rate of 2°C/min. to a hold temperature of 177°C (350°F). Voltage changes across a 100 kilo-ohm resistor were measured during cure on a Hewlett Packard Model 7132A two-pen recorder at a chart speed of 6 inches/hr. The resulting trace of voltage as a function of time is described and analyzed in Section III.

II.3.b Audrey Dielectrometer

The dielectric monitor, or Audrey II, impresses an alternating voltage across a capacitor in which the resin of interest is the dielectric. The dissipation factor of the capacitor and the capacitance are measured and recorded as a function of time. The Audrey II system has an AC frequency range of 100 Hz to 1000 Hz and may be fixed at any frequency in this range or repetitively swept over this range

The circuitry is not described here, but a block diagram, Figure 2, indicates component relationship. Basic components of Audrey II are shown in the photograph of Figure 3.

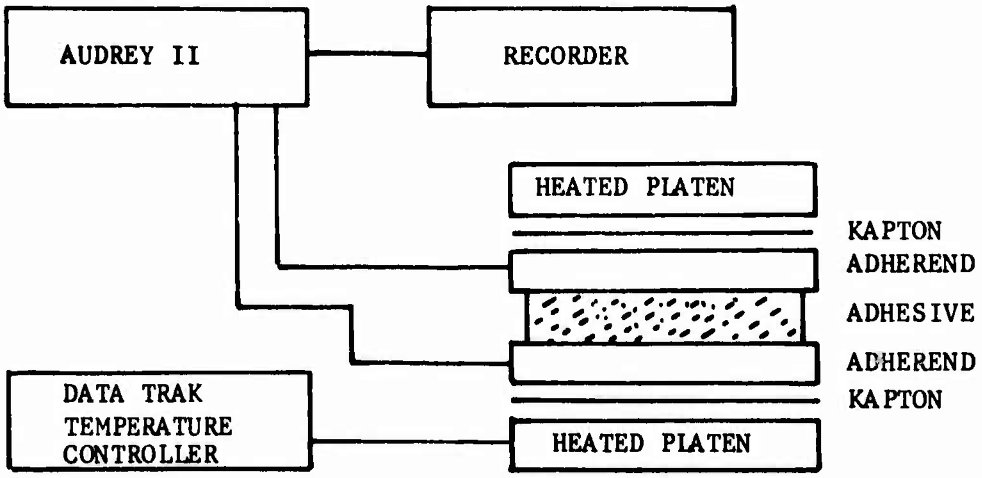


Figure 2. Audrey II Block Diagram

The Data Trak temperature controller indicated in the block diagram above is a card programmable controller that is capable of controlling laboratory presses and hot plates. Virtually any production encountered heating rate can be duplicated. This unit was used extensively throughout the program.

The basic Audrey unit used in the initial phases of the work has a floating ground system. This requires that the adherend specimens be electrically isolated from common grounds such as heater platens. Kapton film (0.005 inches) provides excellent isolation over the temperature ranges of interest. Earlier LMSC studies showed this technique did not introduce additional dielectric changes. Audrey curves, i.e., dissipation factor and capacitance vs. time, for both adhesive systems in single lap shear joints are described and analyzed in Section III.

During the course of the program two modifications were made on the Audrey at LMSC's expense. The first incorporated a common ground mode, referred to as the monoprobe technique, which eliminates numerous ground loops and increases the signal-to-noise ratio. The second modification permits direct reading of phase angle and vector voltage. However, the impressed voltage is still limited to one volt. Neither of these modes were explored in sufficient detail to impact the present program and more work along these lines appears warranted.

II.3.c Phasemeter

The method used for monitoring phase angle and vector voltage was basically designed by D. Mayberry of Mayberry Associates of El Cajon, California. It has the advantage that all of the components are off-the-shelf items. As shown schematically in Figure 4, an audio oscillator (Hewlett Packard Model 200CD) impresses an AC signal (10 volts) through a reference resistor and an adhesive sample to ground. A value for this resistor is empirically chosen to provide a satisfactory signal response. For all the experiments described herein, a resistance of 100 kilo-ohm was

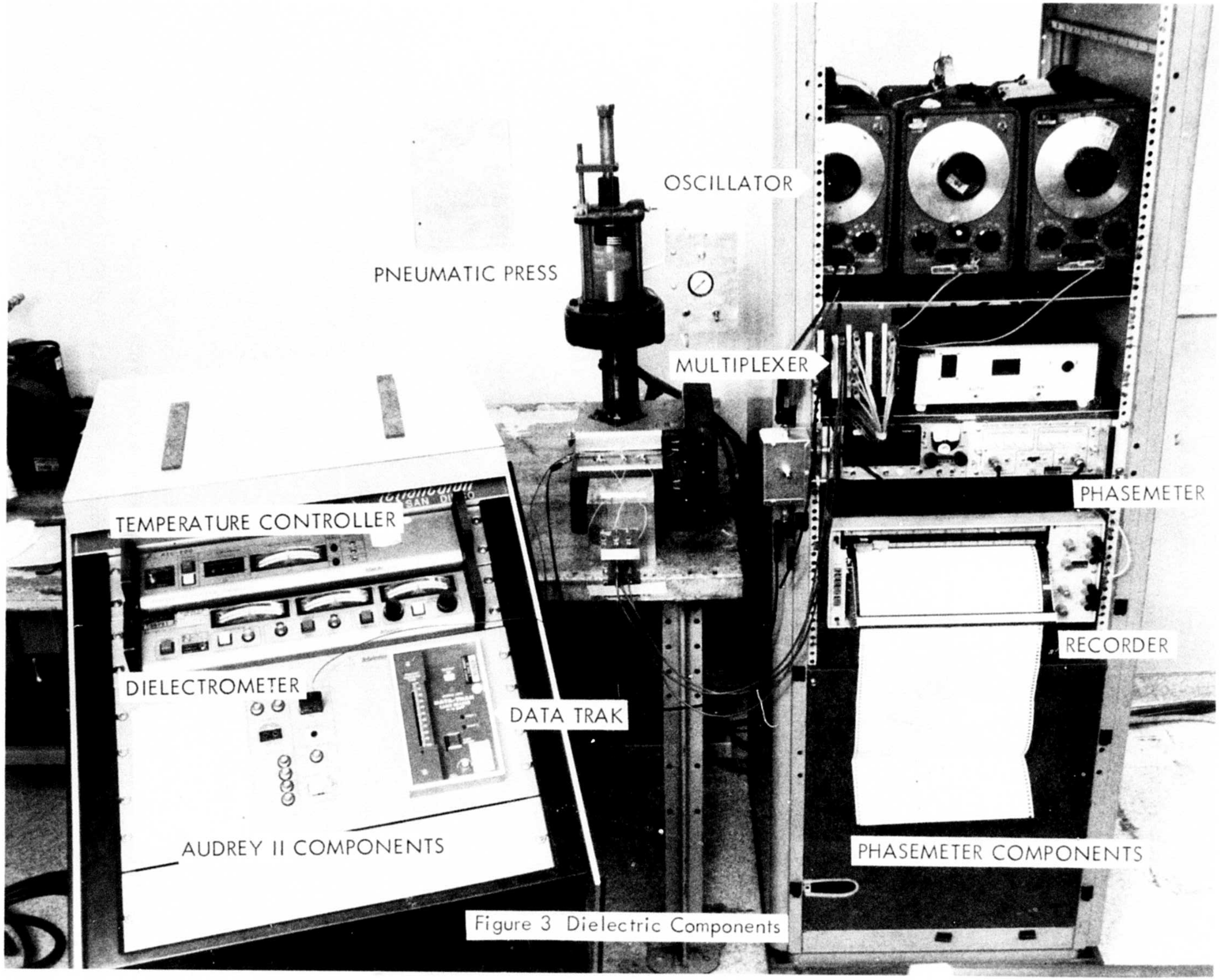


Figure 3 Dielectric Components

used. Phase angle and vector voltage are measured with a phasemeter (Dranetz Model 305-PA-3009) and plotted as a function of time on a two-pen recorder (Hewlett Packard Model 7132A). A photograph of the phasemeter set up where the Audrey Data-Trak is used for controlled heating rates is shown in Figure 3. The measured phase angle is not equal to but is related to the phase angle across the sample.

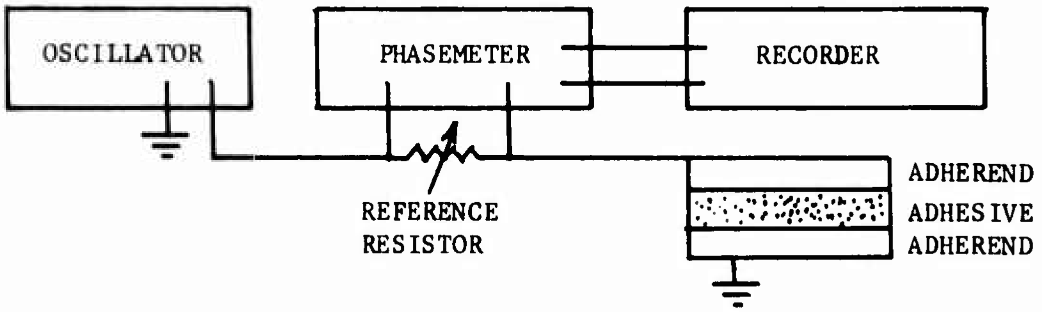


Figure 4. Phasemeter Schematic

This method affords several advantages over the basic Audrey II unit: (1) a higher voltage capability, 10-15 volts vs. 1 volt, which results in a higher signal-to-noise ratio, (2) a wider frequency range, 5 Hz to 600 kHz vs. 100 Hz to 1 kHz, and (3) a common ground for both monitoring system and processing equipment which makes electrical isolation easier.

Phasemeter traces following cure in both individual lap shear specimens and panels bonded with both FM-73 and PL-729 adhesives are described and analyzed in Section III.

II.4 Monitoring Configurations

Three basic approaches for introducing leads from the monitoring instrumentation to the adhint were investigated during this program. These are, herein, referred to as direct, external and internal probing, each requiring a different monitoring configuration consistent with dielectric lead isolation requirements and adherend conductivity. In this section, each configuration is described and its suitability with aforementioned dielectric methods is discussed. This is done first for flat adherend overlap joints, many of which were mechanically tested, and then for honeycomb sandwich structures.

II.4.a Flat Adherend Configurations

The direct probing approach in which adherends are used as electrodes was used to monitor adhesive cures between conductive adherends in a small pneumatic press. This method worked very well with laboratory size specimens and was demonstrated for both aluminum and graphite/epoxy composite adherends. As illustrated in Figure 5, adherends are electrically isolated from the grounded platens by Kapton film and from the adherends, extending beyond the confines of the press, with alligator clips. All three monitoring methods are compatible with this configuration. When used with either the phasemeter or the iongraphing methods only one of the adherends need be isolated from the platen. However, two isolating sheets of Kapton were used in all experiments to maintain uniform heating and electrical characteristics.

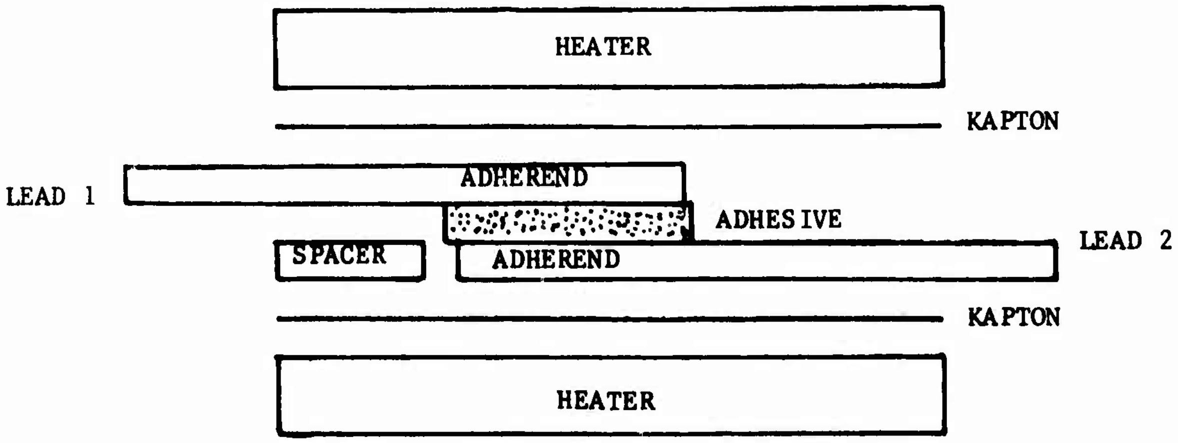


Figure 5. Direct Probing Configuration

The <u>external</u> approach was only partially successful for monitoring the cure between both conductive and non-conductive adherends. Conductive adherends required insulation between each of the copper foil electrodes (1" x 1" x 0.004" (2.5 x 2.5 cm x 0.1 mm) with tag leads) and the adjacent adherends as shown in Figure 6(a). This configuration was used to monitor

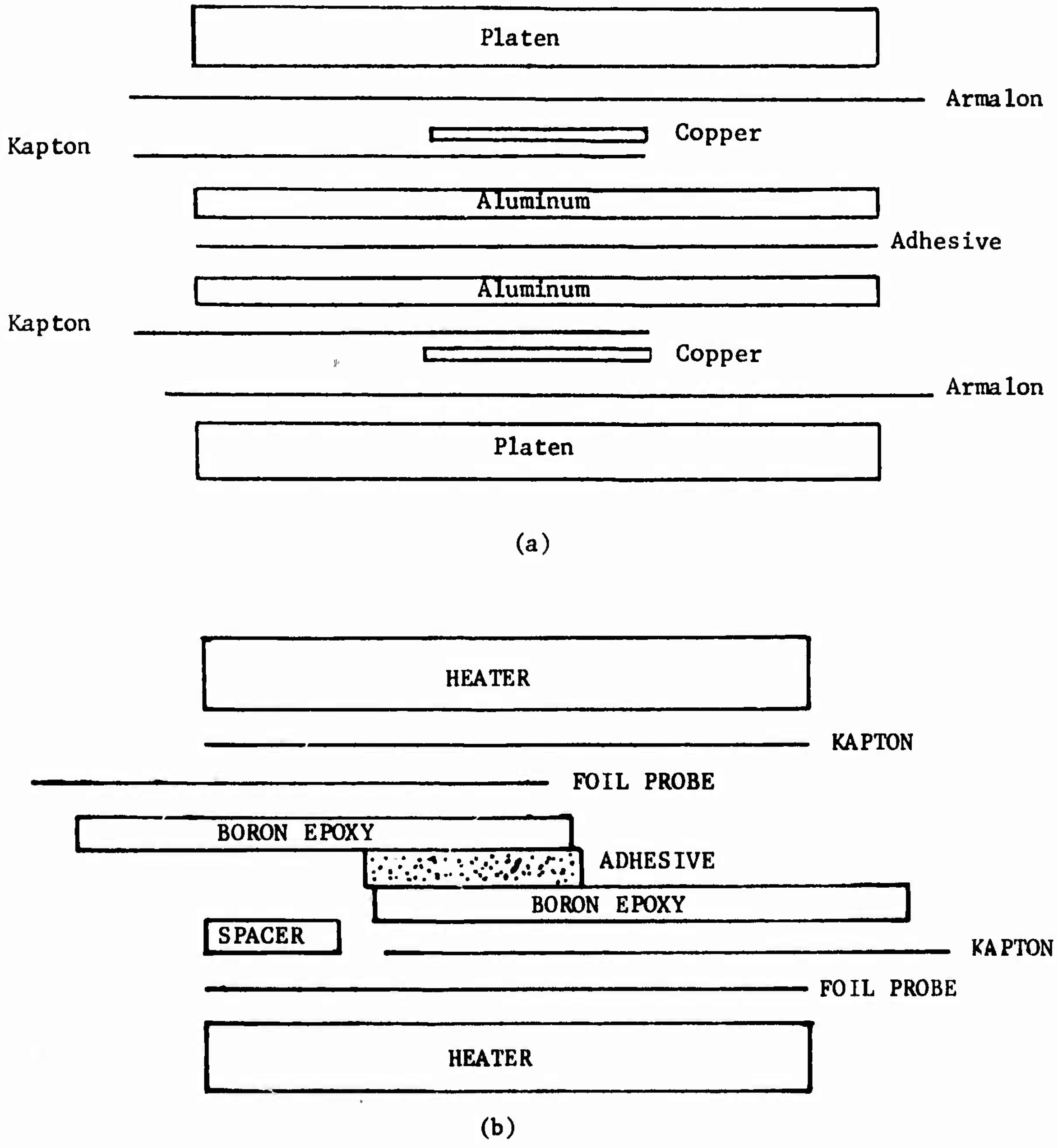


Figure 6. External Probing Configurations

FM-73 cured between 4" x 4" aluminum plates, with the phasemeter technique. A similar configuration, shown in Figure 6(b) was used to monitor cure between boron/epoxy (non-conductive) adherends also using the phasemeter. The only difference between the two configurations is the insulating layer between each lead and adherend is not required for a non-conducting adherend.

Unlike either of the above approaches, the internal approach is new. It was conceived and developed at LMSC during the course of this program. As shown in Figure 7, a foil probe is embedded directly in the bondline between two layers of adhesive film. The probe remains in situ permanently.

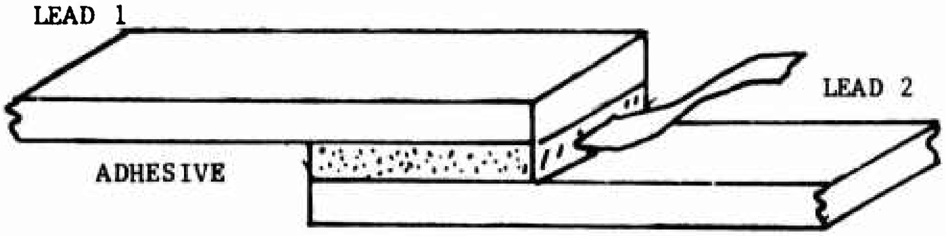


Figure 7. Foil Probe in Bondline

The configuration used for the internal approach for press bonding is shown in Figure 8.

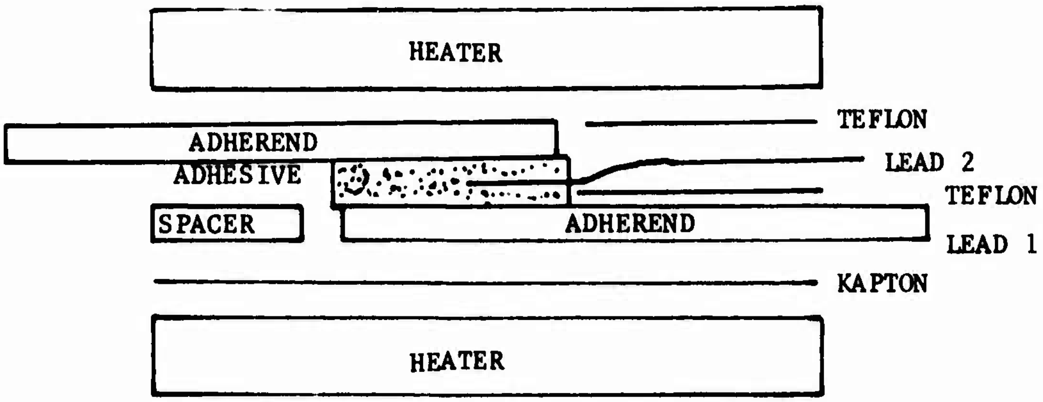


Figure 8. Internal Probe Monitoring Configuration for Press Bonding

As indicated in this figure, the probe must be isolated from both adherends and platens, but only one adherend need be isolated from ground—in this case, a platen. This configuration is compatible with the basic Audrey II grounding requirements. When using either iongraphing or the phasemeter methods, the Kapton film on the lower platen may be eliminated.

This approach was used for monitoring numerous lap shear test specimens both individually and in panels where several probes in the same bondline were simultaneously monitored (see Section II.5 - Simultaneous Cure Monitoring). Monitoring cures between aluminum and titanium adherends were demonstrated with the internal approach and the phasemeter.

II.4.b Honeycomb Sandwich Configurations

Both direct and internal approaches were demonstrated by monitoring honeycomb sandwich cures with the phasemeter method. Aluminum face sheets were bonded to aluminum honeycomb with the FM-73 adhesive on a hot plate.

Three different lead arrangements are illustrated in Figure 9. The

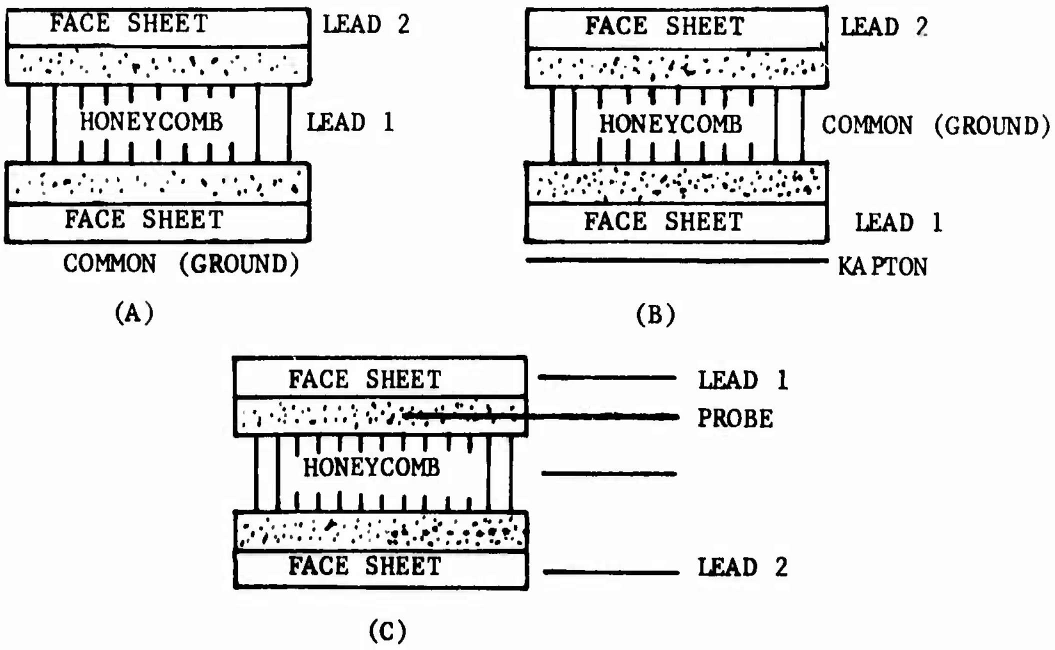


Figure 9. Honeycomb Monitoring Configurations

configuration shown in Figure 9 (A) provided two leads which were simultaneously monitored by employing a switching mechanism as described in the following section. The monitoring signal from lead 1 followed the progress of cure in the lower bondline, whereas the signal from lead 2 related to both upper and lower bondlines. This is a direct approach in that leads are attached directly to the adherends. A second direct approach is depicted in Figure 9 (B) in which sequentially monitored signals from leads 2 and 1 followed cure progress in the upper and lower bonds, respectively. For the combined internal/direct approach illustrated in Figure 9 (C), the additional signal obtained from lead 1 (probe) followed cure at one specific location in the upper bondline.

An attempt at monitoring a cocured honeycomb sandwich panel was made using graphite/epoxy prepreg and an aluminum core honeycomb. A direct probing approach in which leads were attached to each prepreg face was used. Outer prepreg surfaces were faced with Kapton sheets before the panel was cured on a hot plate. Although this initial trial at monitoring cocured honeycomb panels was unsuccessful, further efforts are warranted.

II.5 Simultaneous Cure Monitoring

Cure schedules for FM-73 and PL-729 adhesives require approximately three hours, including heat-up and cool-down times. A desire to monitor several independent lap shear specimens during the same cure cycle prompted the use of a sequential switching device. A Mayberry 10 channel multiplexer, when connected between the dielectric monitor and sample leads, sequentially scanned each sample lead for a preset time interval. This experimental approach expanded our ability to monitor many more cure histories than otherwise possible, greatly reducing the development time for successful monitoring techniques.

Once the internal monitoring configuration evolved, large test panels including eight probed sites were made up for mechanical testing. The multiplexer was used to sequentially monitor cures at each of these sites, as shown schematically in Figure 10.

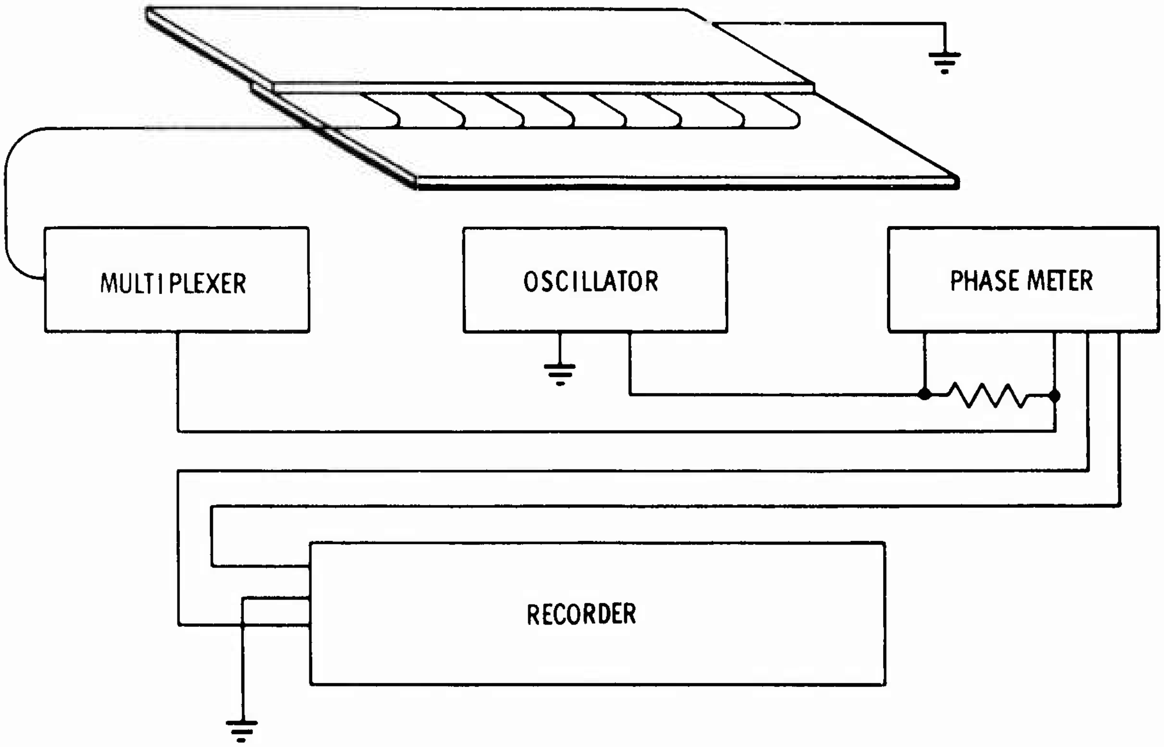


Figure 10. Multiprobe Monitoring Arrangement

In order to facilitate handling eight individual probes, a device called a probe handler was developed. A photograph is shown in Figure 11. Based on LMSC experiences in the fabrication of flexible circuitry, it was fabricated from .005" Kapton, clad on one side with .002" copper foil. The foil was etched to form pads for contacting the aluminum probes. The Kapton was folded so that the copper would contact both faces of the probe while the Kapton provided electrical insulation for the leads. Polyimide covered 22 gauge wire soldered to the copper leads through areas where Kapton was selectively removed provided connections to the multiplexer. High temperature (450°F) solder was used. A standard acrylic adhesive was used to tack the folded faces of the Kapton together, thus limiting their separation and facilitating handling. A pressure strip of silicone rubber was taped (Teflon tape) to one side of

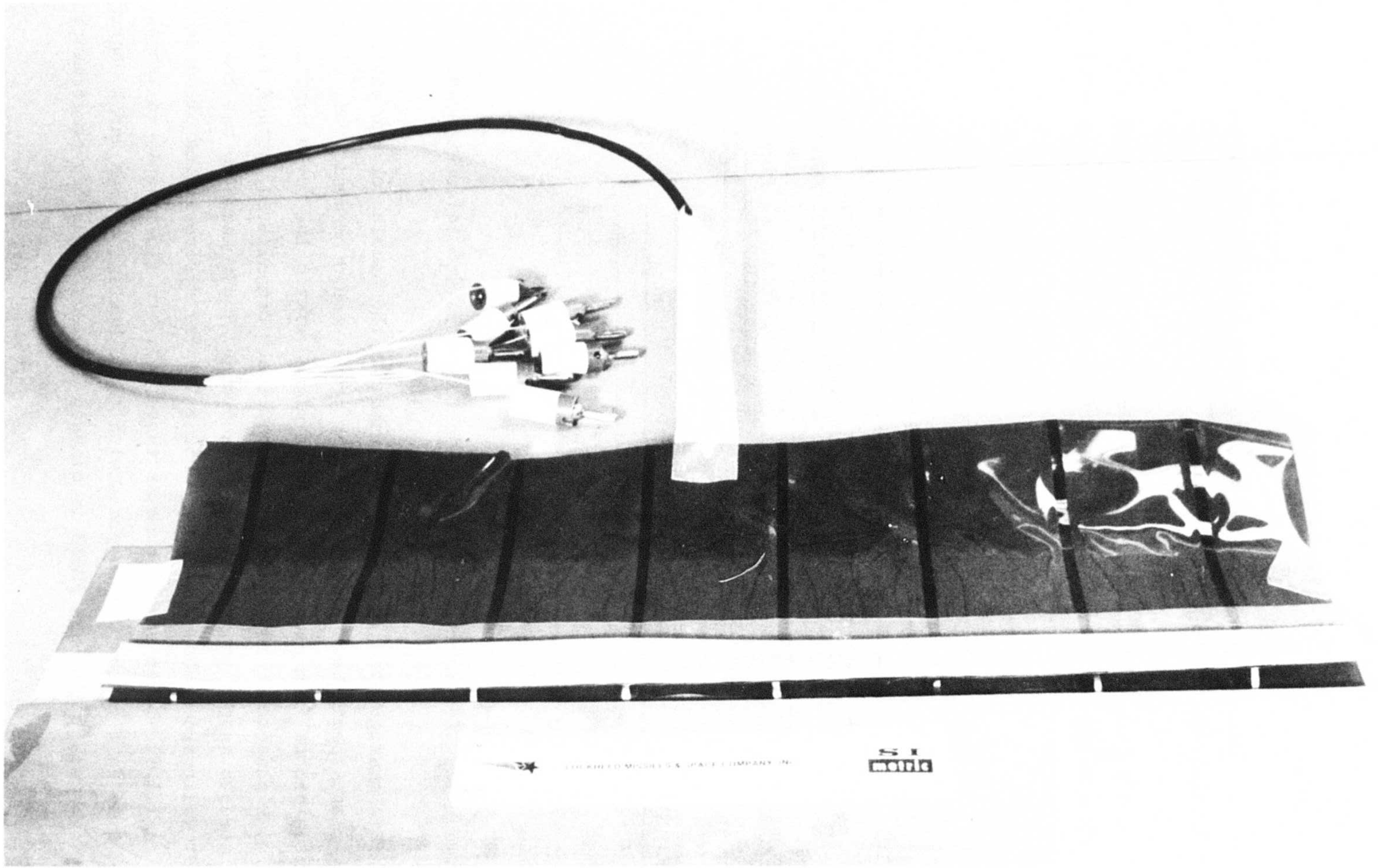


Figure 11 Probe Handling Device

the pad area to ensure good contact between pads and probes when the press was closed. This device continued to function well after repeated use at cure temperatures of 350°F (177°C).

The multiplexer and probe handler were also used for sequentially monitoring multiple probe sites in each of two different adhesive bondlines as shown schematically in Figure 12.

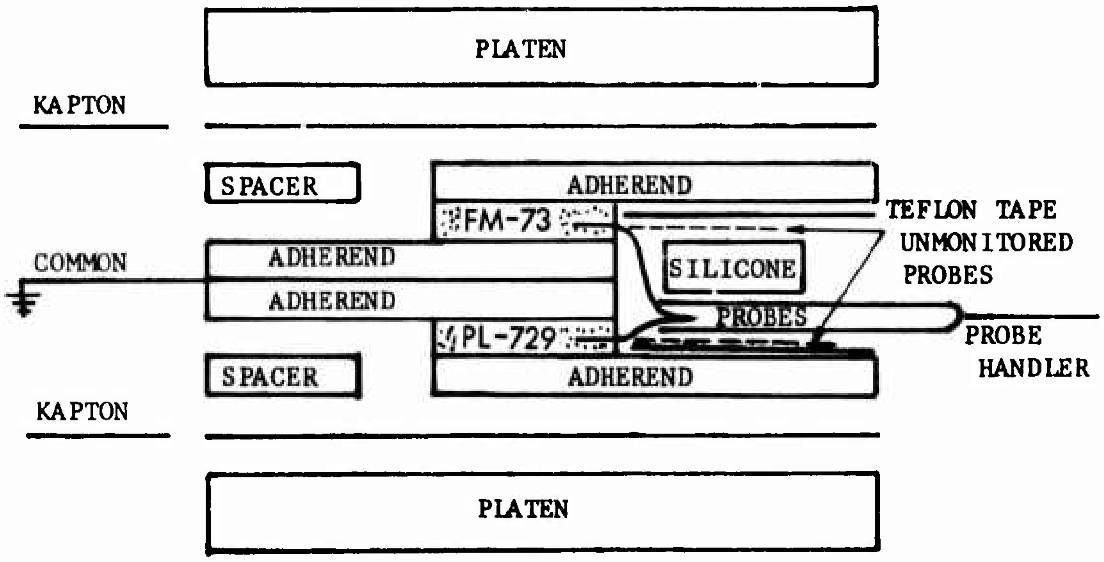


Figure 12. Sequential Multiprobe Monitoring in Two Adjacent Bondlines

This configuration was used for preparing the panels for the environmental test specimens. Since only eight probes could be monitored, alternately selected probes from each bondline were placed within the probe handler. This gave four phasemeter monitorings per bondline. Unmonitored, probed sections were used to supply additional test specimens. Their geometry was the same as for monitored probes which may account for the discrepancies discussed in Section III.3. Large panels such as these, 45.7 cm (18 inches) in length, were cured in a 75 ton Wabash press with timed heating cycles and a controlled cool-down rate. Although FM-73 is classed as a 121°C (250°F) performance product, vendor recommendations include curing up to 177°C (350°F).

II.6 Preparing and Testing Lap Shear Coupons

Adherends were carefully prepared once it was realized that unfinished edges caused monitoring difficulties. Grounding or shorting out of the electrodes must be carefully avoided during cure monitoring. It was found early in the experimentation that rough shear edges were sufficient to short electrodes. Normal shop deburring operations, either sanding, filing or burnishing eliminated most of the problems.

Aluminum foil probes were cut from sheets of aluminum foil using a razor blade and a straight edge. Edges were carefully flattened by burnishing with a smooth wooden dowel. Probes were wiped clean with MEK and then primed in the same manner as the adherends. Titanium probes were similarly prepared.

Adhesive strips were cut 1.58 cm (0.625 inches) wide and pressed onto primed adherends so that .158 cm (0.063 inches) extended from each side of the bondline 1.27 cm (0.150 inches) wide. This ensured adequate fillets after cure. When foil probes were used they were pressed onto the adhesive and they extended 1.1 cm (0.44 inches) into the bondline. Probe sections in the bondline were isolated from the adherends by applying a layer of adhesive, above and below the probes, in these particular areas only.

Curing was carried out according to the supplier's recommendations. FM-73 was cured between 121°C (250°F) and 177°C (350°F) with the bulk of the work being done at 177°C (350°F). All PL-729 cures were at 177°C (350°F). In no case did the bonding pressure exceed the 40 psi recommended by the manufacturers. Heating rates to cure temperatures were programmed between 2°-5°C (3.6°-9°F)/Min. using the Data Trak for all preliminary experiments in a small pneumatic press. Larger scale bonding operations were carried out in a product press using the available heating rate (3.3°C (6°F)/minute) as indicated on the individual curves.

The few titanium coupons which were tested and some aluminum coupons tested in the initial phases of the program were made from individually machined 2.54 x 10.16 cm (1 x 4 inches) adherends. Test coupons used for both the investigation of probe width on bond strength and for environmental testing were cut from 45.7 cm (18 inches) wide panels.

As shown in Figure 12 of the previous section, environmental panels were monitored in pairs. Probe positions, monitoring sequence and lap shear specimen locations are indicated for individual panels in Figure 13. Probes were spaced so that alternate lap shear specimens cut from each panel contained probes. Seventeen specimens were thereby obtained from each panel. The alpha-numeric labels given to each specimen indicate the monitoring sequence (0 through 8) and whether or not the bondline was probed (P or N).

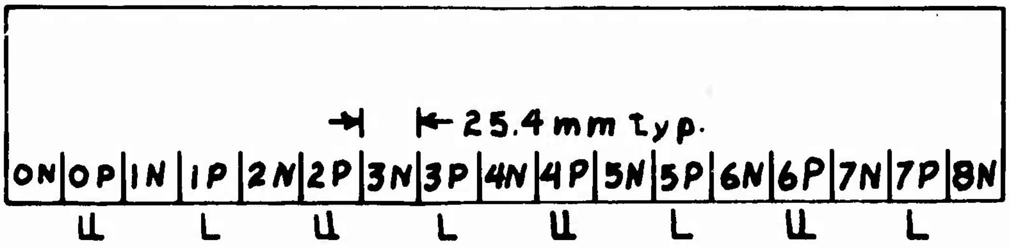


Figure 13. Panel Monitoring Sequence and Specimen Location (N - unprobed; P-probed)

Baseline specimens (ON, OP, 4N, 4P, 7N, 7P, 8N) were mechanically tested without prior environmental exposure whereas the remaining specimens (1N, 1P, 2N, 2P, 3N, 3P, 5N, 5P, 6N, 6P) were environmentally exposed and then tested.

Lap shear bond strengths were determined on 1.27 cm (0.5 inches) overlap specimens of nominal 2.54 cm (1.0 inches) width in general accordance with the provisions of ASTM Standard D1002.

II.7 Environmental Tests

Environmental tests were conducted on both probed and unprobed bondlines. Lap shear test specimens were exposed to the environments described below and then mechanically tested along with control specimens from the same panel. A minimum of 10 coupons per adhesive (5 probed, 5 unprobed) were subjected to each exposure condition. The exposure conditions were:

1. 24-hour distilled water boil
2. 7-day immersion in distilled water at ambient temperature
3. 30-day immersion in distilled water at ambient temperature
4. 200 hours at 95% RH at 48.9°C (120°F)

All tests were conducted in accordance with Federal Test Standard Methods 175A. Environmental tests were run solely with 2024-T3 aluminum adherends. No attempts were made to protect edges or passivate the aluminum in any way other than by priming in the immediate vicinity of the bondline. This provided the most extreme test conditions for the bond since in good production practices bonds are filleted and covered with moisture resistant coatings.

II.8 Neat Resin Characterization

II.8.a Mechanical Properties

Tensile and flexural mechanical properties were determined from castings of both supported and unsupported FM-73 and PL-729 adhesives. Castings were made by first vacuum degassing the adhesives, then curing them in a mold according to the same schedule used for bonding environmental test panels, i.e., at approximate 2.5°C (5°F)/minute heat up rate to 177°C (350°F) followed by a one hour hold at temperature.

PL-729 was degassed after stacking individual layers in a 12.5 cm (5 inches) x 17.8 cm (7 inches) x 0.254 cm (0.100 inches) rectangular mold. Thirty minutes at 65°C (149°F) and 27 inches Hg were sufficient to produce relatively void-free castings after the one hour 177°C (350°F) cure. Supported FM-73 was more difficult to degas and completely void-free castings could not be made. However, quite surprisingly, these voids seemed to have little effect on the mechanical properties as judged by comparison of strengths for samples having fracture surfaces with and without voids. Effective area reduction was probably less than 3%.

Tensile measurements were made in accordance with FTMS 406, Method 1013 and flexural measurements in accordance with FTMS 406, Method 1031.

II.8.b Wetting Angle Measurements

Wetting angles were measured by visual observation of an adhesive in contact with a surface of interest using a Kayeness ellipsometer. A schematic diagram is shown in Figure 14.

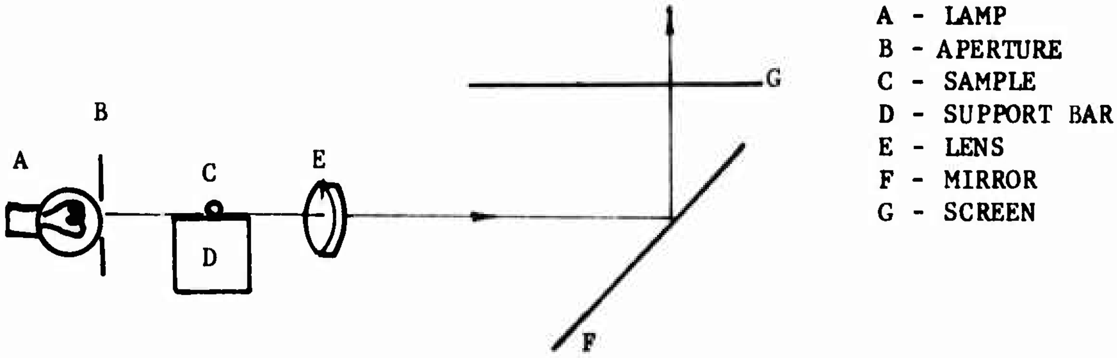


Figure 14. Schematic for Wetting Angle Determinations

An image of the sample (C) is projected on a screen (G) and the angle between substrate and resin is measured with a protractor. Adhesive flow rates are slow enough so that reading can be easily made by manual operation.

The equipment as supplied has a chrome-plated bar as a sample support (D). However, for our operations the support bar was replaced with a transite bar containing a 30 watt cylindrical heater (Figure 15). The transite support was also equipped with thermocouples for temperature readings and clamps so that various substrates of interest could be firmly attached. Using the Data Trak and the ATC-200 Controller from the Audrey it was possible to measure wetting angles at the same heating rates used for the dielectric measurements and the bonding experiments. Measurements were generally taken every 2-5 minutes until no further changes occurred.

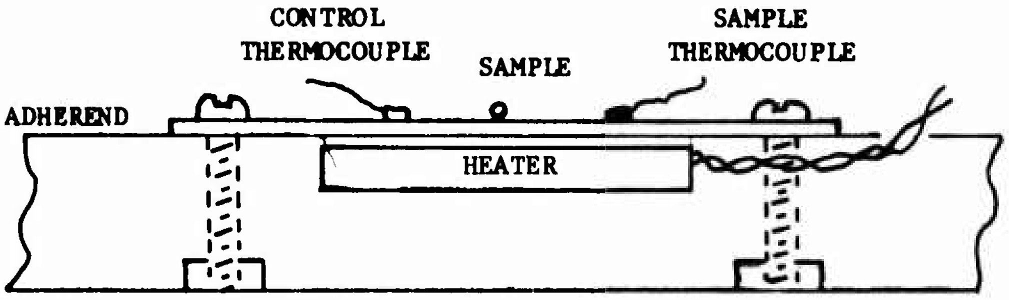


Figure 15. Alternate Support Bar

II.8.c Differential Scanning Calorimetry

A 990 Series Du Pont Thermal Analyzer with DSC attachment was used for studying adhesive cure rates and determining glass transition temperatures. Typical sample sizes were twenty milligrams. Detailed operating procedures may be found in the manufacturer's instruction manual. The Du Pont 990 heat programming system also permitted a heating rate match between DSC analysis and dielectric analyses, wetting angle measurements and bonding operations.

Section III

RESULTS AND DISCUSSION

III.1 Evaluation of Dielectric Methods

In order to compare the dielectric methods, each was used to monitor the same adhesive bonding process by which aluminum adherends were bonded with PL-729. A 1.27 cm (0.5 inches) overlap bond measuring 2.54 cm (1.0 inches) in width was monitored. Electrical leads were attached directly to the adherends which were appropriately isolated. Adhints were heated at approximately 2°C (3.6°F)/min. to 177°C (350°F) and held at temperature for the duration of the test.

In the following section, monitoring results are analyzed individually before they are compared. The physical significance given to these curves is discussed in Section III.5.

III.1.a Iongraphing

Iongraphing monitoring results are shown in Figure 16 where voltage changes across a reference resistor are shown as a function of time. Voltage begins to increase as the adhesive softens and then gradually decreases as the adhesive cures. The peak indicates a region of minimum viscosity immediately followed by the onset of cure. The significance of the long decay time is unknown since only a one hour hold at 177°C (350°F) produces a T_g of 177°C (350°F) in the DSC. The method appears insensitive to any dispersion peaks prior to softening. Perhaps the biggest drawback with respect to production monitoring is adequately defining the gel point in the region of the very gradual voltage decrease where cure begins.

Note the irregular heat-up rate and heating in excess of 177°C (350°F) due to a faulty temperature controller.

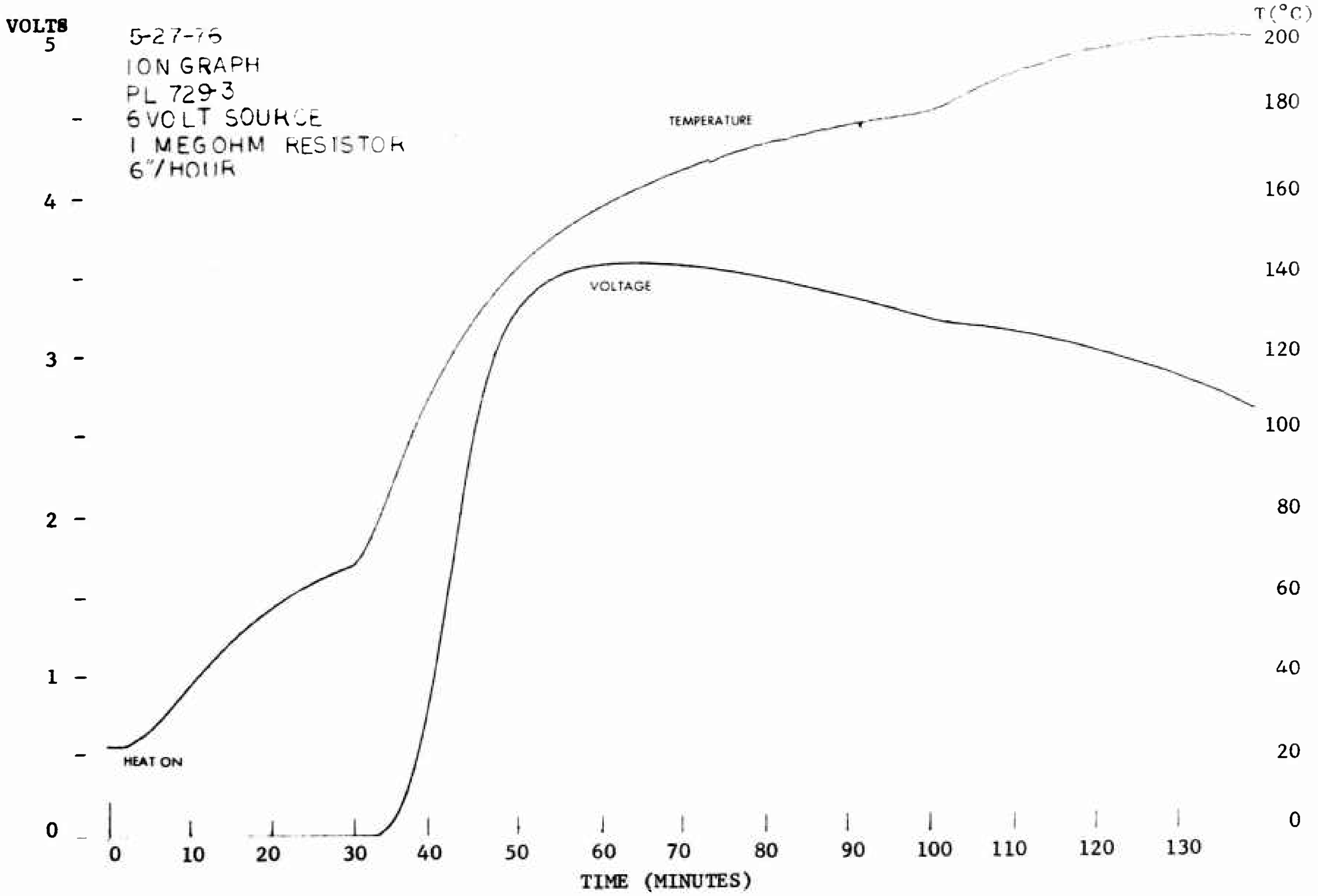


Figure 16. Iongraphing Trace

III.1.b Audrey II Dielectrometer

Audrey monitoring results for PL-729 measured at a frequency of 1 kilohertz at an applied voltage of one volt are shown in Figure 17 where capacitance and dissipation are plotted as a function of time. Three well-defined peaks are evident in the dissipation curve. The origin of the first at 44°C (111.2°F) is a matter of speculation, although wetting angle measurements at the same heating rate indicate that it is associated with softening. Further, PL-729 is known to contain a nitrile elastomer of the type which exhibits a pseudo -crystalline change at 44°C (111.2°F). The second dissipation peak at 80°C (176°F) indicates a major softening of the adhesive. The following minimum indicates a region of minimum viscosity prior to the onset of cure. A sharp rise leads to a cure-associated dissipation peak which reflects the T_g of the adhesive at that particular stage of cure. The curve then decays to a constant value in a time that agrees quite well with physically acceptable times for completion of cure.

III.1.c Phasemeter

Phasemeter monitoring results measured on PL-729 at a frequency of 1 kilohertz and 10 volts are shown in Figure 18 where phase angle lag and vector voltage are plotted as a function of time. Two dispersion (dissipation) peaks are indicated. The first is associated with softening and the second with cure. In between peaks is a region of minimum viscosity followed by the onset of cure.

III.1.d Comparison of Dielectric Methods

Monitoring curves which were analyzed in the preceding sub-sections are shown superimposed on a common time scale in Figure 19. A qualitative comparison may thus be made.

The iongraphing curve contains the least information but it is also the least demanding in terms of equipment. Since a DC power source is used,

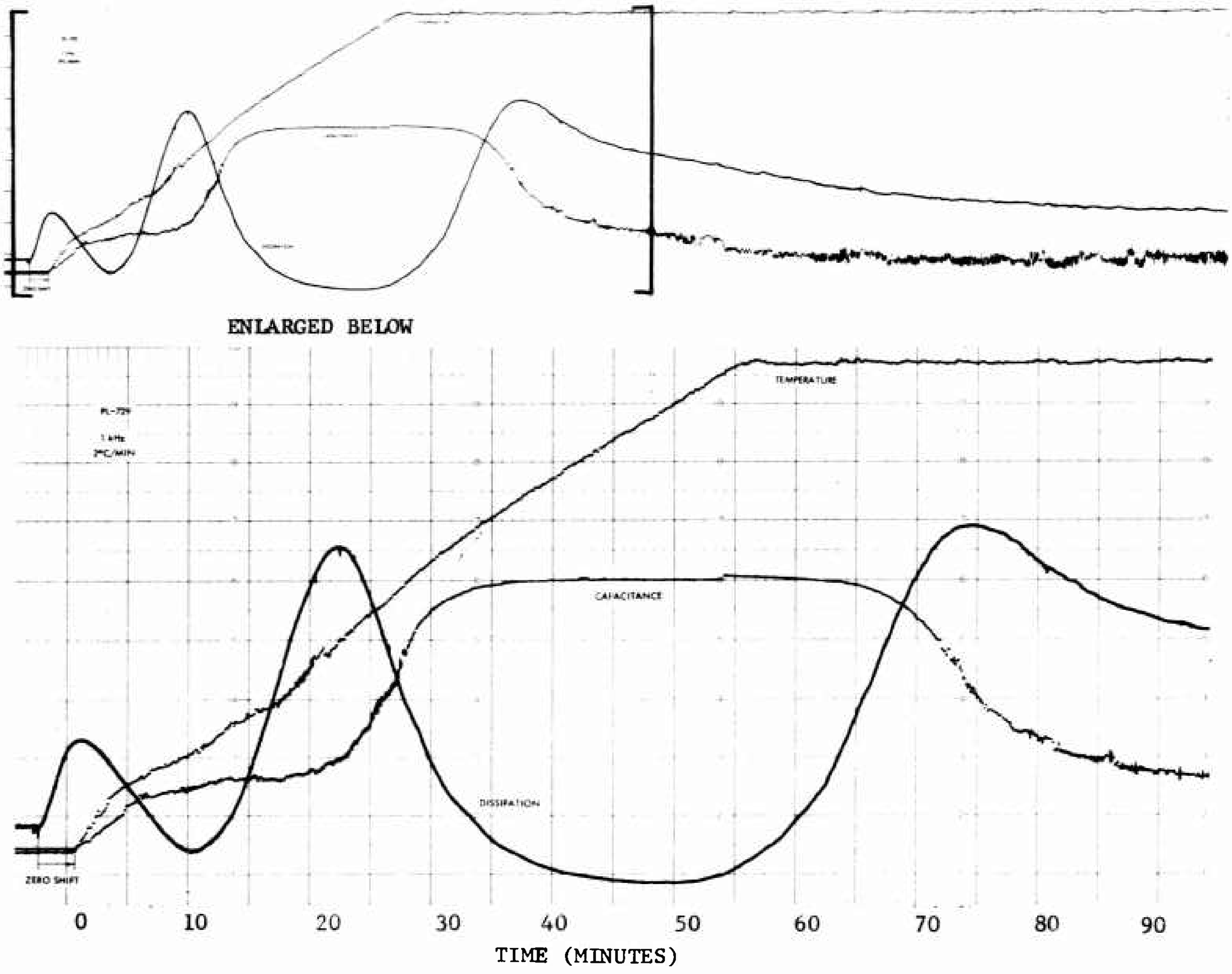


Figure 17. Audrey Monitoring Trace

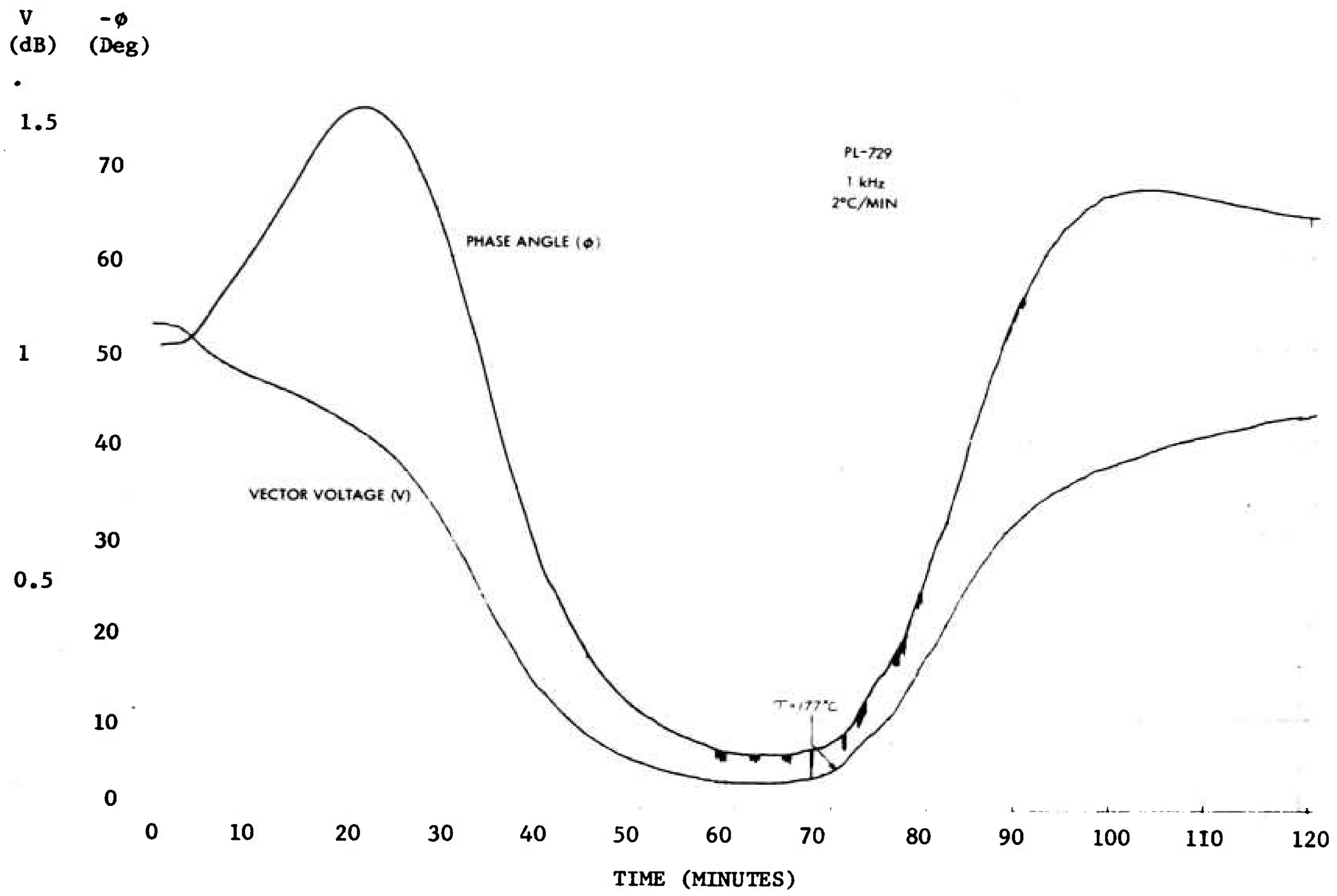


Figure 18. Phasemeter Monitoring Trace

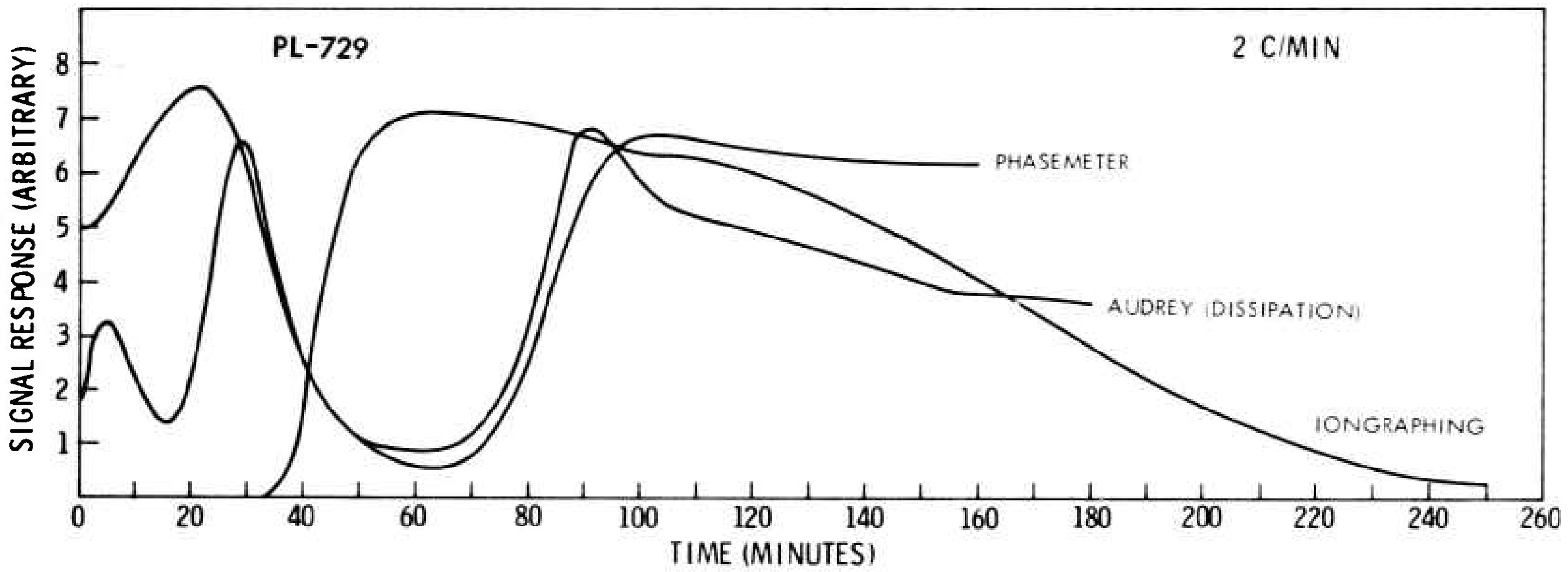


Figure 19. Comparison of Dielectric Monitoring Traces

a strong signal which is not affected by stray electrical noise is obtained. Although dispersion peaks associated with softening are absent, a sharp rise in voltage correlates fairly well with the flow regions indicated by Audrey and phasemeter traces. Comparable times are indicated in all three curves for the minimum viscosity and the onset of cure. However, the iongraphing curve is less definitive in the area where important events of the cure are occurring. Herein lies the main drawback of iongraphing. As is evident from the comparison Figure 19, iongraphing continues to indicate progress of cure far beyond completion times indicated by the other two methods. As already mentioned, the significance of this is unknown and bears further investigation.

The Audrey monitoring method appears to be the most sensitive with PL-729. Two softening peaks are clearly defined as opposed to only one by the phasemeter. The cure associated peak is also better defined with the Audrey than with the phasemeter. The Audrey II is a fine laboratory tool but the circuitry makes it difficult to adapt to a production environment. Specifically, demanding isolation requirements and a somewhat low signal-to-noise ratio constitutes the main deficiencies.

The phasemeter trace contains all the essential information offered by the Audrey including definition of the softening region, minimum viscosity, onset of cure and completion of cure. The main advantage of the phasemeter method for production applications is the higher signal voltage and relaxed electrical isolation requirements.

As a result of this comparison the phasemeter method was selected for monitoring all cures through the duration of the program.

III.2 Monitoring the Adhesive Bonding Process

The phasemeter method was used to monitor FM-73 and PL-729 adhesives cured between flat adherends of aluminum, titanium, graphite/epoxy composite and boron/epoxy composite. Honeycomb sandwich panels consisting of aluminum honeycomb core, face sheets of either aluminum or graphite/epoxy prepreg, and FM-73 adhesive were also monitored by this method. The results are discussed below.

III.2.a Aluminum Adherends

Four individual lap shear bonds, two of each adhesive, were simultaneously monitored using the direct probing approach in a small pneumatic press heated at 4.7°C/minute (8.6°F). Phase angle lag and vector voltage were monitored as shown in Figure 20 and in Figure 21 where the run was repeated. Note that the phasemeter data displayed is the reverse of the convention established by Audrey. The low viscosity valleys normally observed in Audrey measurements appears as peaks in the phasemeter measurements. Future work should probably avoid this issue and conform to a convention consistent with Audrey curves.

The original traces were recorded in two colors so that phase angle and vector voltage can be readily distinguished. In these curves and those which follow each curve has been drawn in for the readers convenience. As noted, the signal responses were strong and the shapes of the curves are quite reproducible. However, quantitative reproductions (peak magnitudes) were not obtained indicating probable differences in bondline dimensions.

The phase angle trace shows softening peaks for both FM-73 and PL-729 adhesives 8.5 minutes into the cure schedule at 55°C (131°F). Softening ceases as network development begins at 23 minutes (130°C) for FM-73 and at 29 minutes (158°C) for PL-729. The peak labelled A' is followed by a monotomic increase in phase angle lag in the case of PL-729. Molecularly this indicates that at this heating rate the T_g continues to increase with the programmed temperature up to 177°C (350°F). The corresponding curve for FM-73 shows a change in inflection at point B when the programmed temperature coincides with the T_g of the developing network. As the programmed temperature

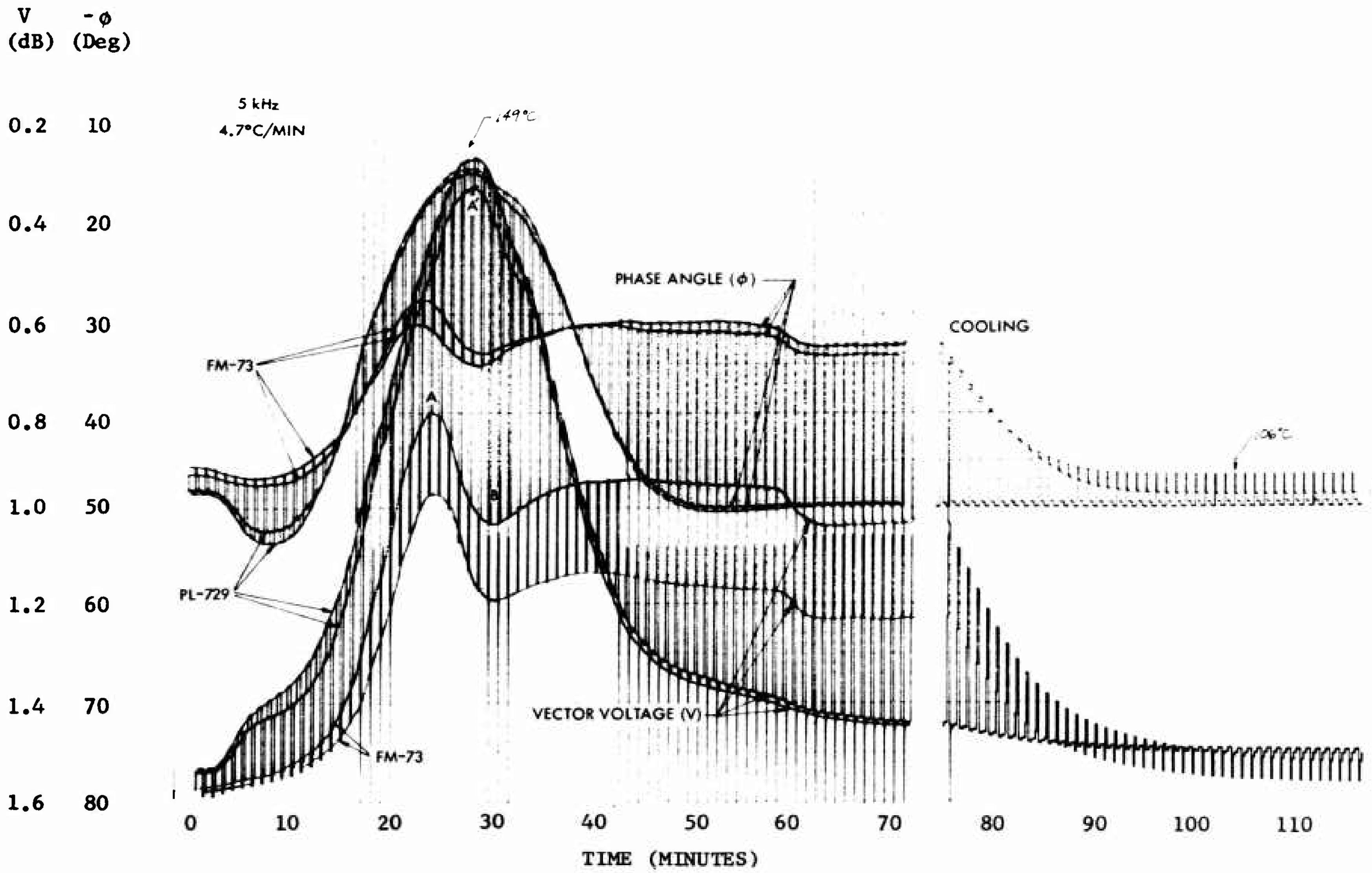


Figure 20. Aluminum Adherend Monitoring Trace

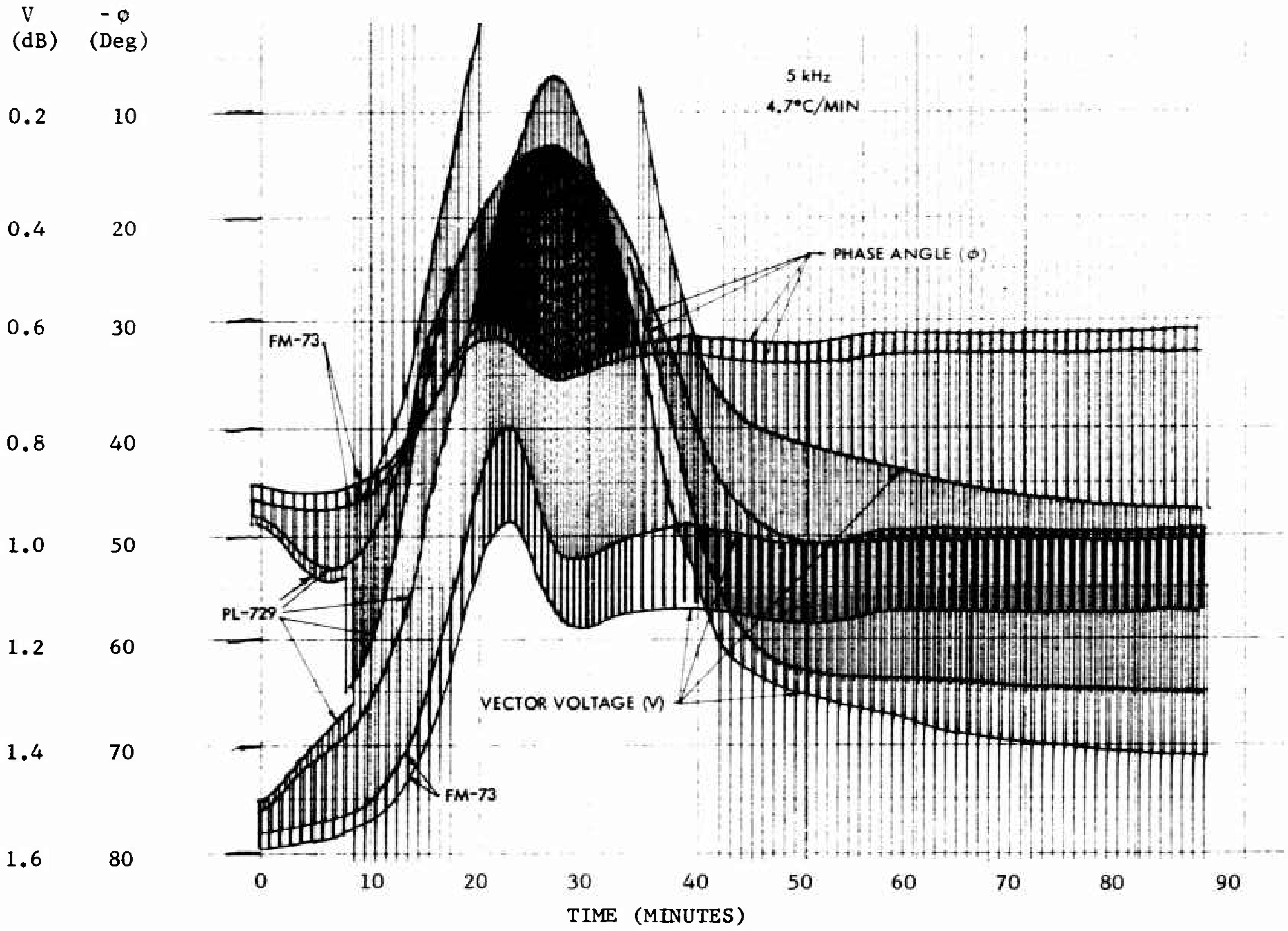


Figure 21. Aluminum Adherend Monitoring Trace, (Repeat-Experiment)

continues to rise above the still advancing T_g molecular mobility increases until the hold temperature is reached and cure is completed. These differences may be used to distinguish the individual adhesives in other monitoring traces with similar temperature histories.

Note that vector voltage seems to be more sensitive to the completion of cure than does the phase angle, especially in the case of PL-729. Note, too, that upon cooling the phase angle and vector voltage change only for the FM-73 adhesive. This, as you may recall, is the 121°C (250°F) service product. It is above its T_g at 177°C (350°F) as is indicated by the dielectric changes measured during cool down.

The external probing approach was also investigated with the phasemeter for FM-73 between aluminum adherends. Copper probes (1" x 1") were separated from the aluminum by Kapton sheets as described in Section II.4.a. When frequencies between 1 and 5 kHz gave no meaningful response, frequencies of 25, 50 and 100 kHz were investigated as shown in Figure 22. The signals are weak and only what appears to be softening could be detected.

It was felt that the feasibility of using external probes in a production environment should be more closely examined before proceeding experimentally. Concern stems from examining the charge path from electrode to electrode in this configuration as follows. The input signal is first diminished by a layer of Kapton. Any charge that does reach the conductive adherend is then distributed over the entire surface so that the charge flux to the second electrode through yet another layer of Kapton, is seriously reduced. Because the charge spreads uniformly over a conductive adherend, the geometry of the adherends comes into play. Not only is the flux proportionately reduced, but the required electrical isolation of both adherends can present difficulties.

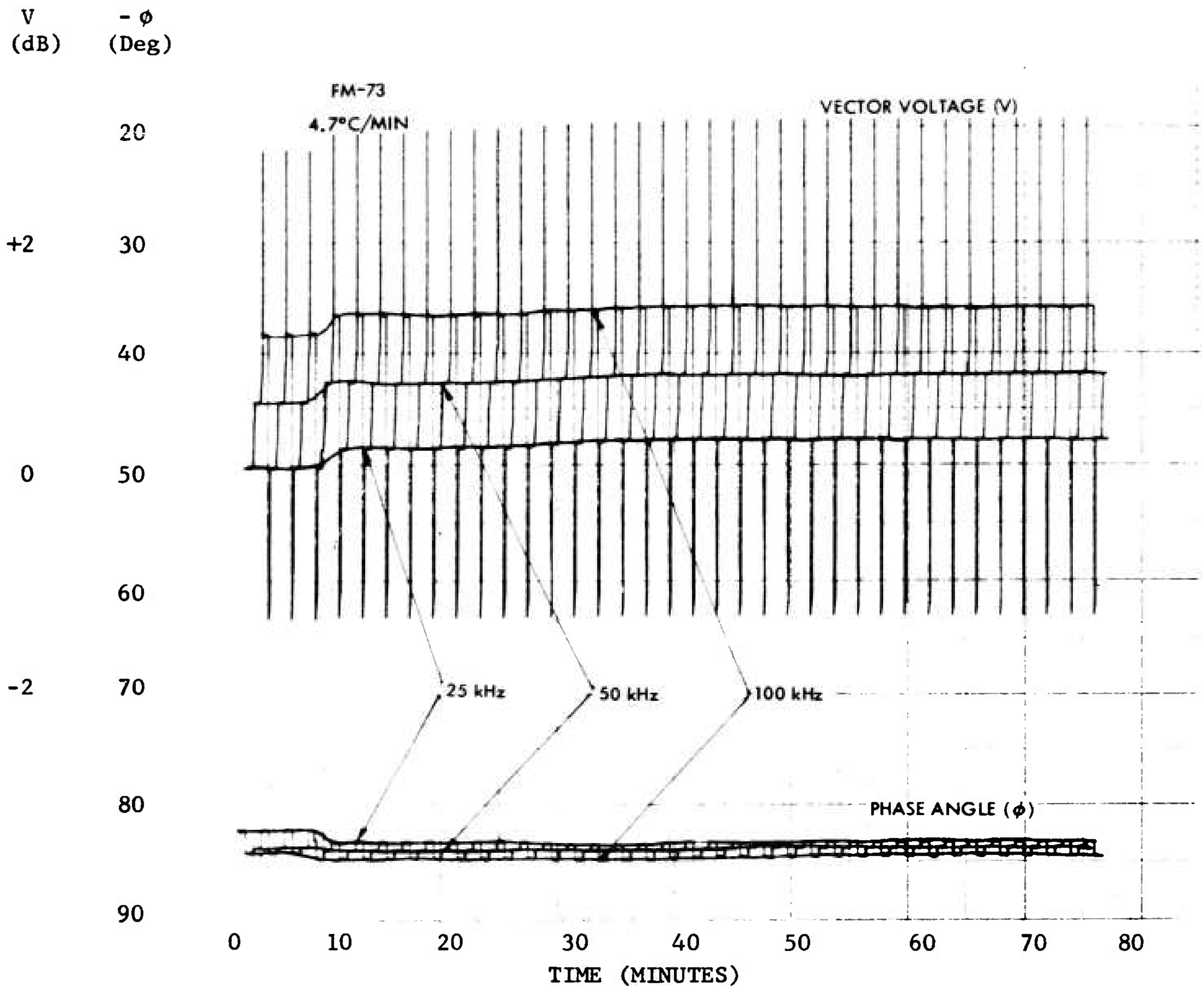


Figure 22. External Monitoring Through Aluminum Adherend

III.2.b Titanium Adherends

Cures of the PL-729 adhesive between titanium adherends were simultaneously monitored for each of four separate bondlines as shown in Figure 23. Two bondlines were monitored with the direct approach and two with embedded titanium probes (0.019 mm thick foil). A 4.7°C/min. (8.6°F) heat-up rate to 177°C (350°F) was used in the small pneumatic press.

As with aluminum adherends, a strong signal was obtained. Both embedded probes shorted to the adherends following adhesive softening and their leads were thereafter deleted from the trace. The same monitoring pattern described for aluminum adherends was obtained here. The lap shear specimens gave the following bond strengths:

With Probe	4750 psi
Without Probe	5020 psi

This indicates that the probe would have minimal effect on bond strength.

III.2.c Graphite/Epoxy Adherends

Four individual bonds, two PL-729 and two FM-73, between graphite/epoxy adherends were monitored with the direct probing approach as shown in Figure 24. A 4.7°C/min. (8.6°F) heat-up rate to 177°C (350°F) was used in the small pneumatic press.

With the exception of lead #4, the same well-defined traces observed with aluminum adherends were obtained. The reason for the unusual trace from lead #4 is unknown.

III.2.d Boron/Epoxy Adherends

One FM-73 and two PL-729 bondlines were simultaneously monitored between boron/epoxy composite adherends. As shown in Figure 25, the individual curves are almost indistinguishable. Since the boron/epoxy

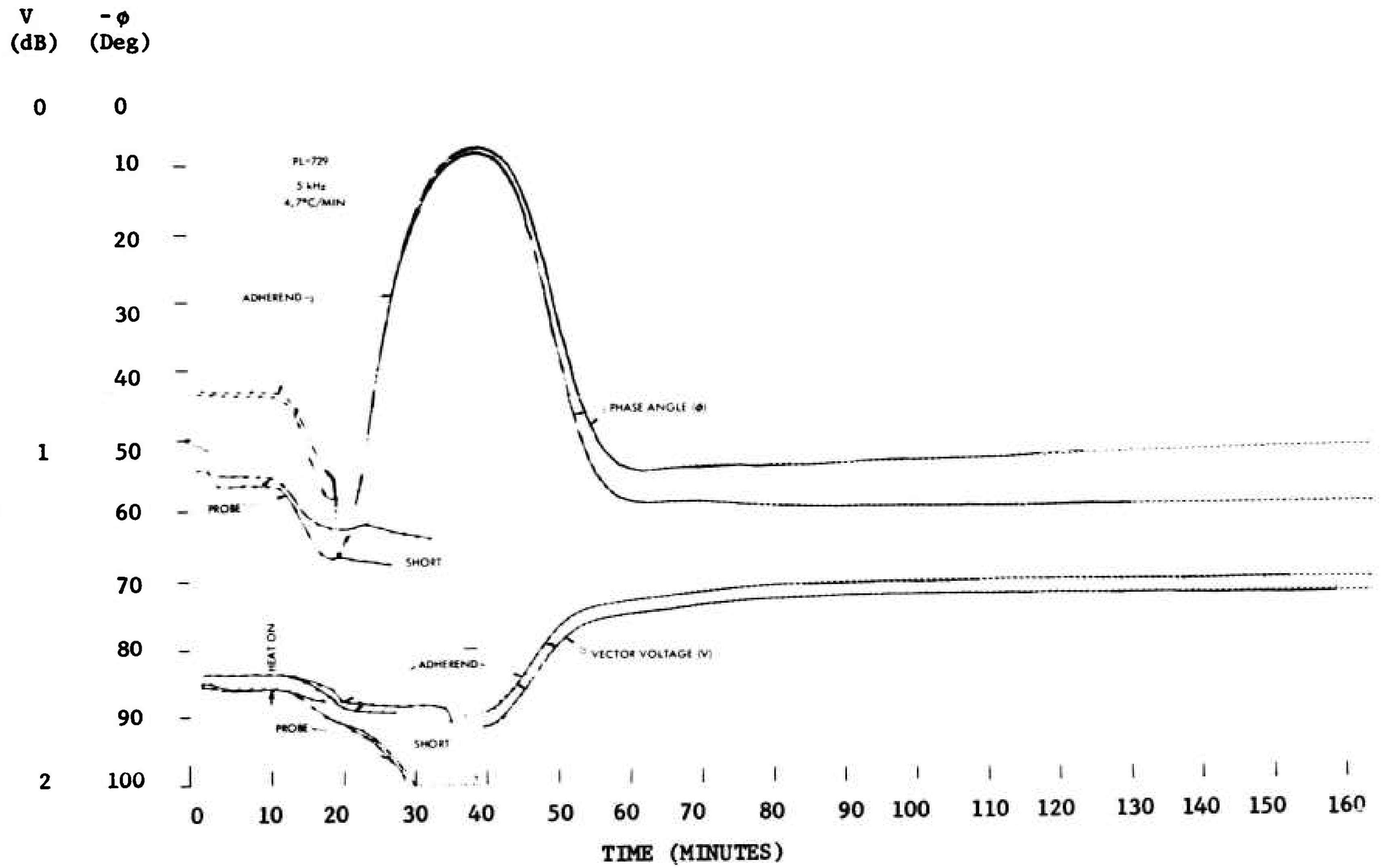


Figure 23. Titanium Adherend Monitoring Trace

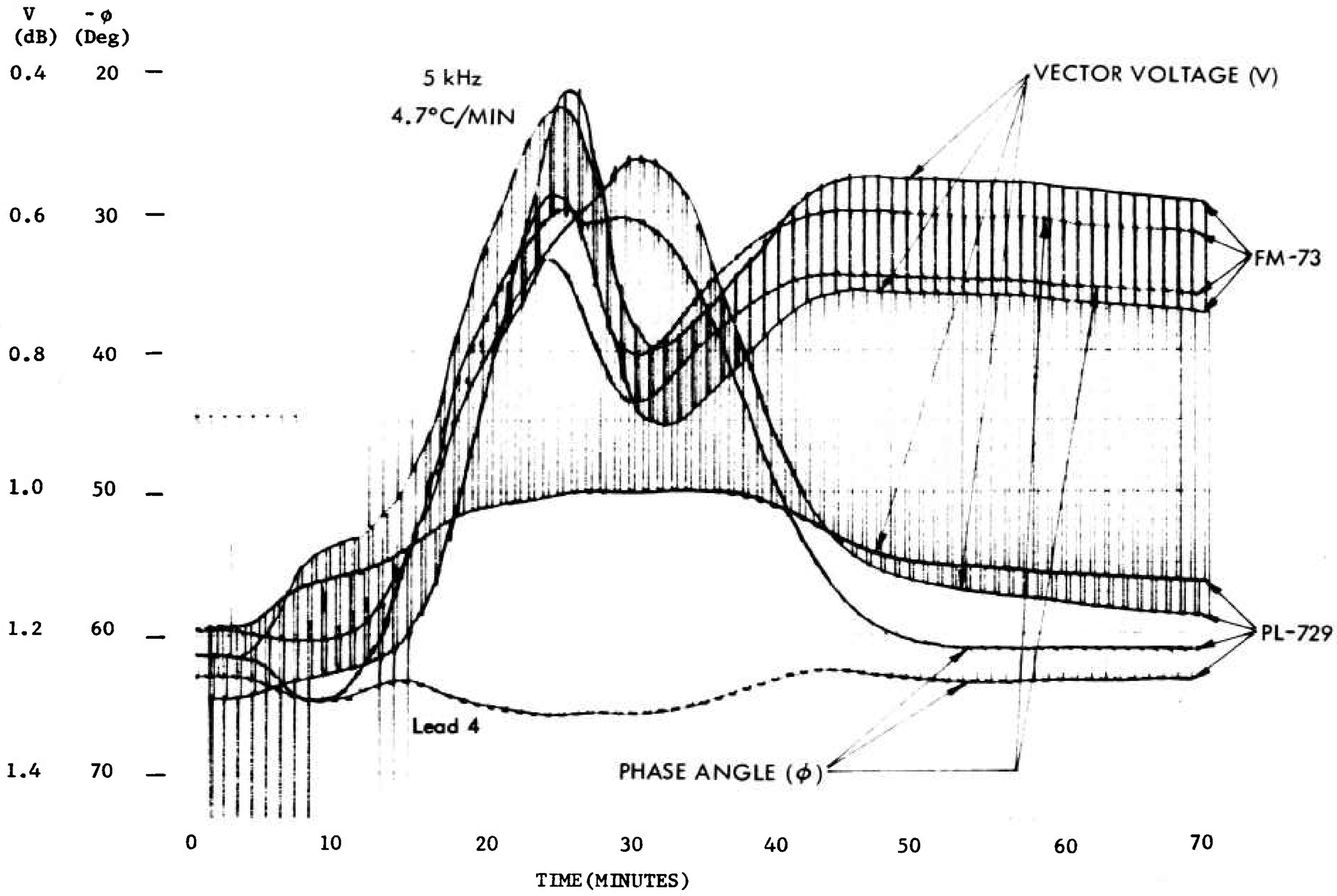


Figure 24. Graphite/Epoxy Composite Adherend Monitoring Trace

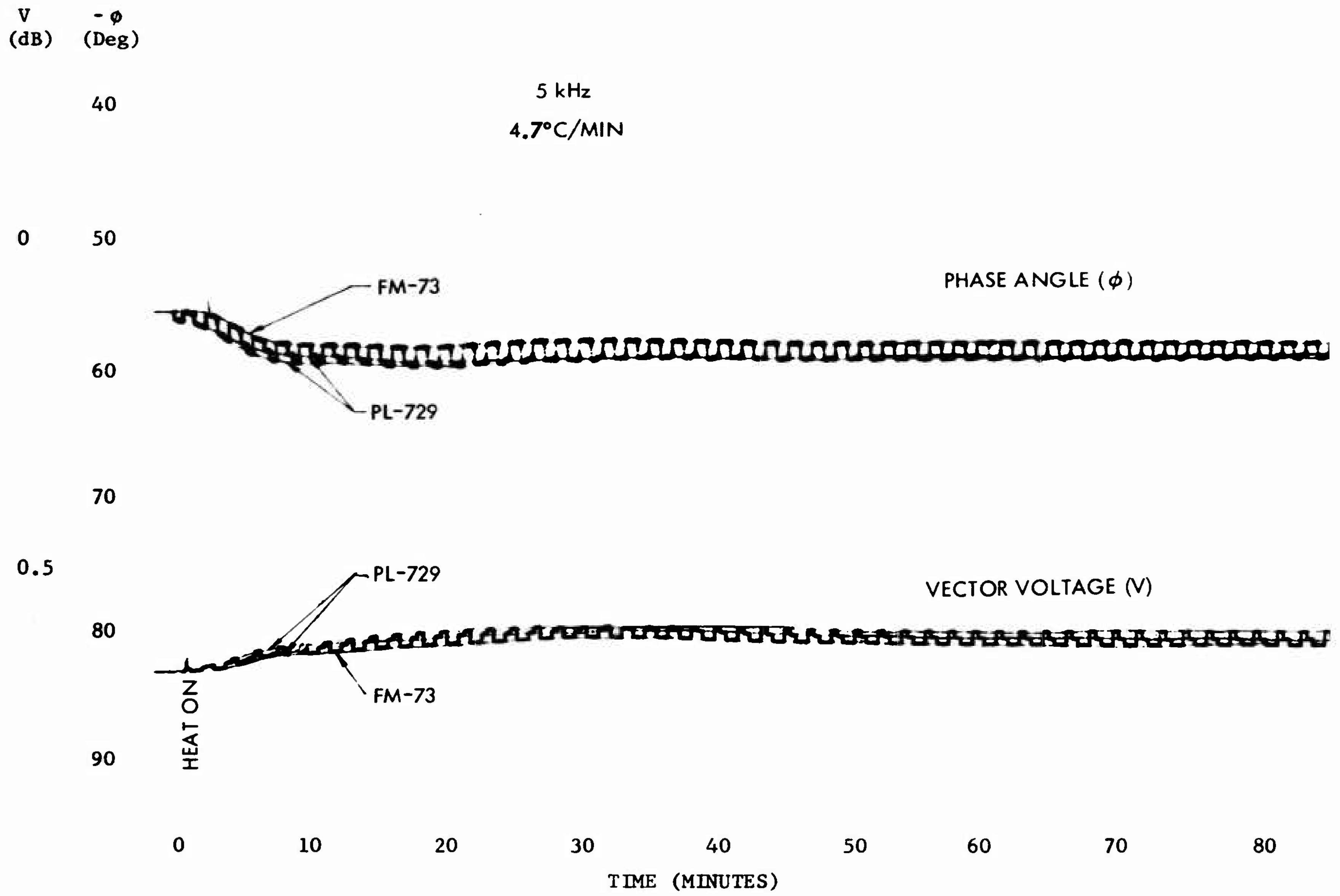


Figure 25. Boron/Epoxy Composite Adherend Monitoring Trace

composite used was non-conductive, despite graphite-core boron fibers, the external probing approach was required. Aluminum foil electrodes were used as described in Section II.4.a.

Although close inspection reveals some changes in phase angle and vector voltage, the signals are too weak to distinguish individual adhesive characteristics.

The external probing approach for non-conductive adherends does not suffer from the more serious problems referred to when discussing conductive adherends, such as aluminum, i.e., surface charge distribution. Increasing the reference voltage and possibly changing the reference resistance may improve signal strength. An internal probing approach may solve this problem but more work is needed to resolve the question.

III.2.e Aluminum Honeycomb

Results obtained with the monitoring configurations described in Section II.4.b are presented for aluminum-core honeycomb bonded to aluminum face sheets with FM-73 adhesive. All honeycomb sandwiches were cured on a hot plate at a heat-up rate of 4.7°C/min. (8.6°F) to 177°C (350°F).

Figure 26 was obtained using the configuration shown in Figure 9A in which the lower face sheet was a common ground. The lead attached to the upper face sheet monitors cure in both bondlines, whereas the lead attached to the honeycomb monitors only the lower bondline. A monitoring frequency of 1000 Hz was used. The trace shows that cure in the upper bondline lags behind cure in the lower one. This is not surprising since heating was from the bottom side only. What is somewhat surprising is the shape of this FM-73 cure curve compared to earlier ones monitored between lap shear adherends. This difference may be readily explained when one realizes that heat conduction through a honeycomb-core is much slower than through a lap shear joint even though the same programmed heating rate was used. In the

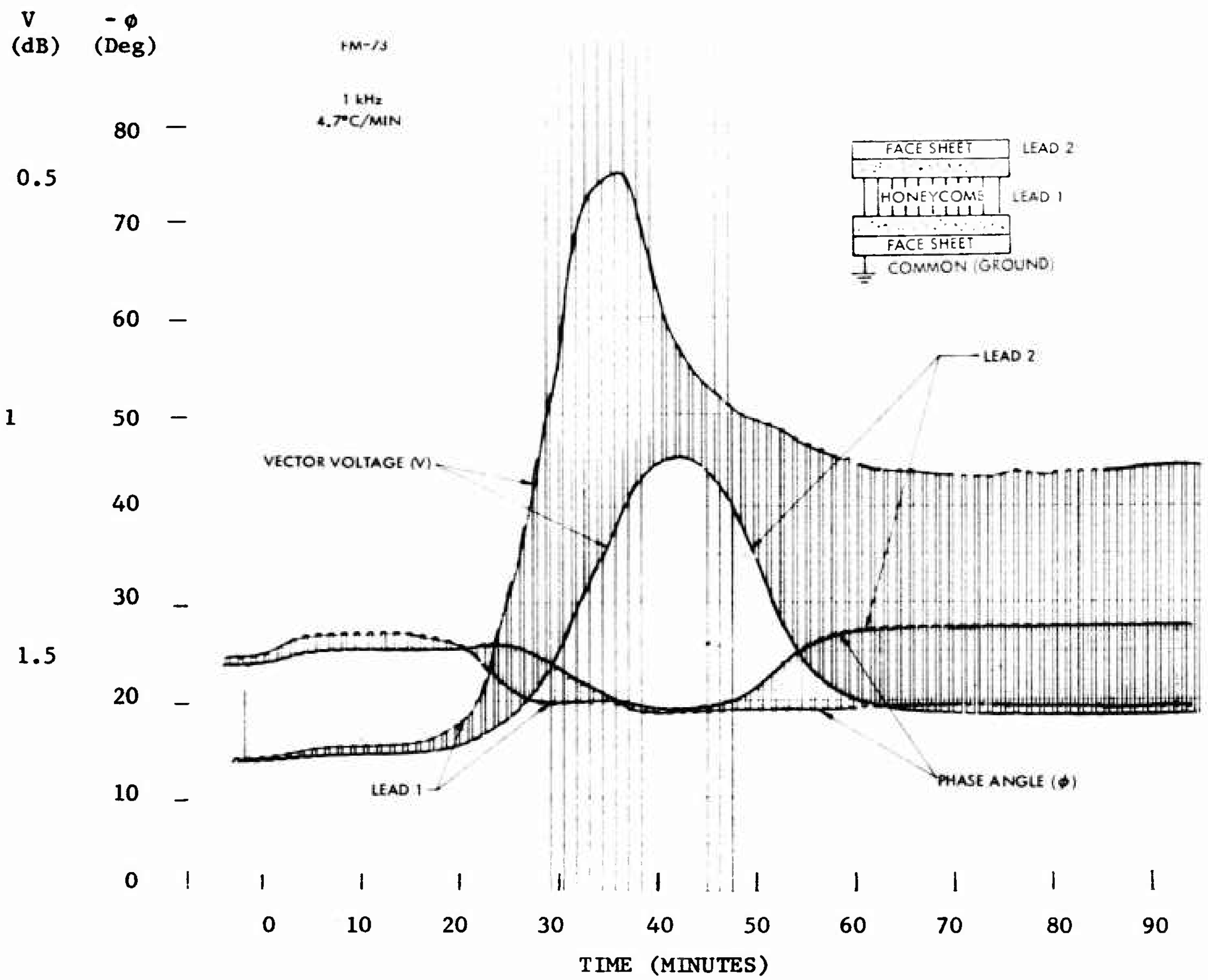


Figure 26. Honeycomb Monitoring Trace 1 kHz

honeycomb geometry the minimum viscosity occurs for leads 1 (honeycomb) and 2 (upper adherend) at 38 and 44 minutes, respectively, as opposed to 23 minutes in the lap shear geometry. Judging from the gradual increase of phase angle lag after 75 minutes the programmed temperature just barely exceeds the T_g of the curing adhesive. It is therefore apparent that the actual temperature in either honeycomb bondline never reached 177°C (350°F).

Figures 27, 28, 29 and 30 were obtained with the monitoring configuration shown in Figure 9B in which the aluminum honeycomb is common. Upper and lower bondlines are individually monitored. Note that shorting was observed in the run of Figure 28 (honeycomb to the upper adherend) between 24 and 30 minutes and again between 41 and 44 minutes. The curve is quite similar to that in Figure 26 at the same frequency once softening begins. Figures 28, 29, and 30 show traces for the same geometry run at frequencies of 2, 5, and 10 kHz. Lead polarities for the phase angle were inadvertently reversed in Figures 29 and 30. Only the trace at 5 kHz which shows a shoulder during softening is different from the rest. In light of the narrow range of frequency over which this is observed, it is somewhat doubtful that the difference is real, but additional experimentation is required for corroboration of frequency effects.

A foil probe was embedded in the upper bondline of a similar honeycomb sandwich and monitored with three leads as illustrated in Figure 9C. The results of this combined direct and internal approach are shown in Figure 31. An experimental oversight caused a lag in the programmed heating rate so that direct comparison with previous traces is not possible. Cure at the specific probe location was somewhat slower than within the upper bondline as a whole. This seems reasonable since the probe was near an edge where heat losses are higher.

The embedded probe approach is well suited for monitoring honeycomb cures in which either the honeycomb or the adherends are non-conductive.

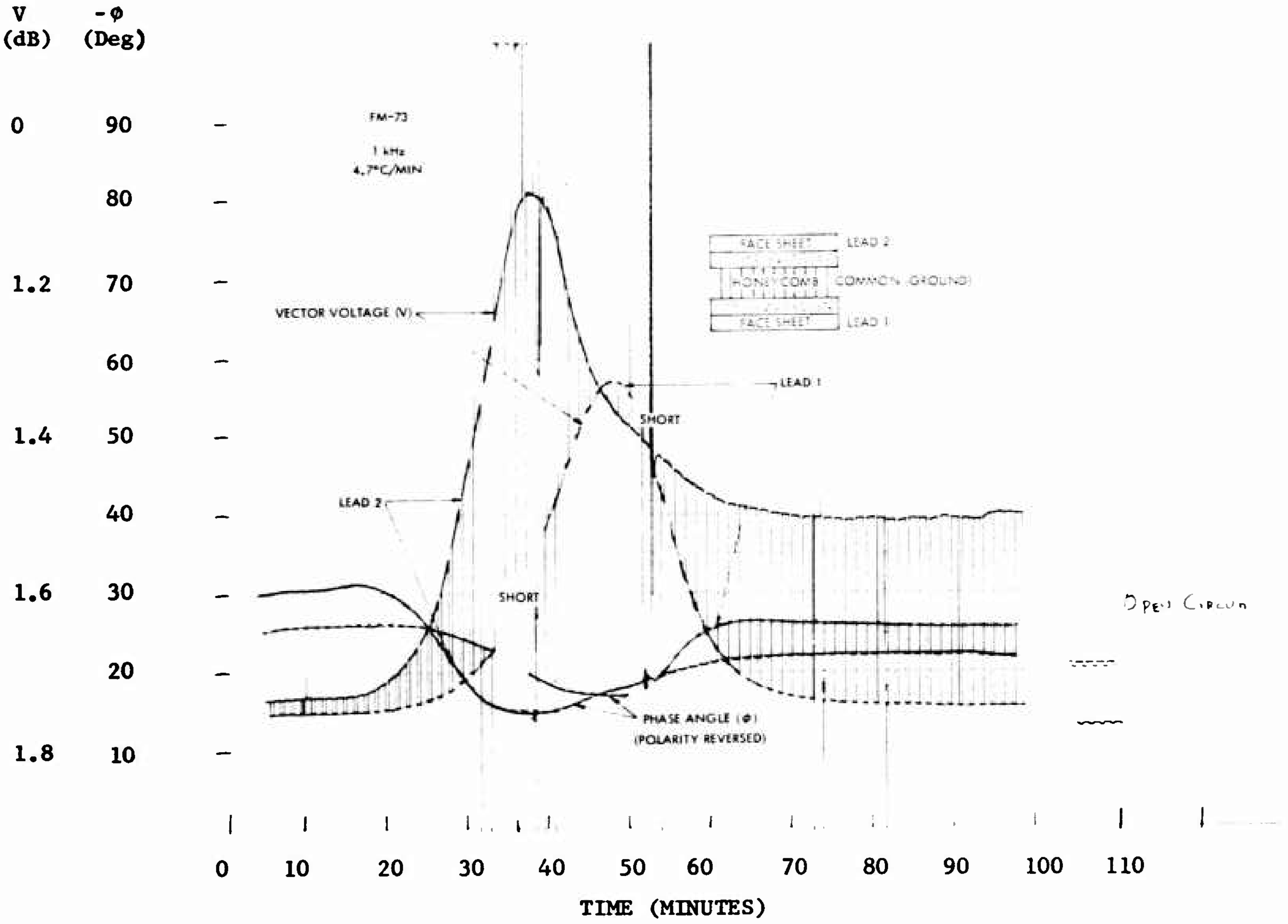


Figure 27. Honeycomb Monitoring Trace 1 kHZ, (repeat)

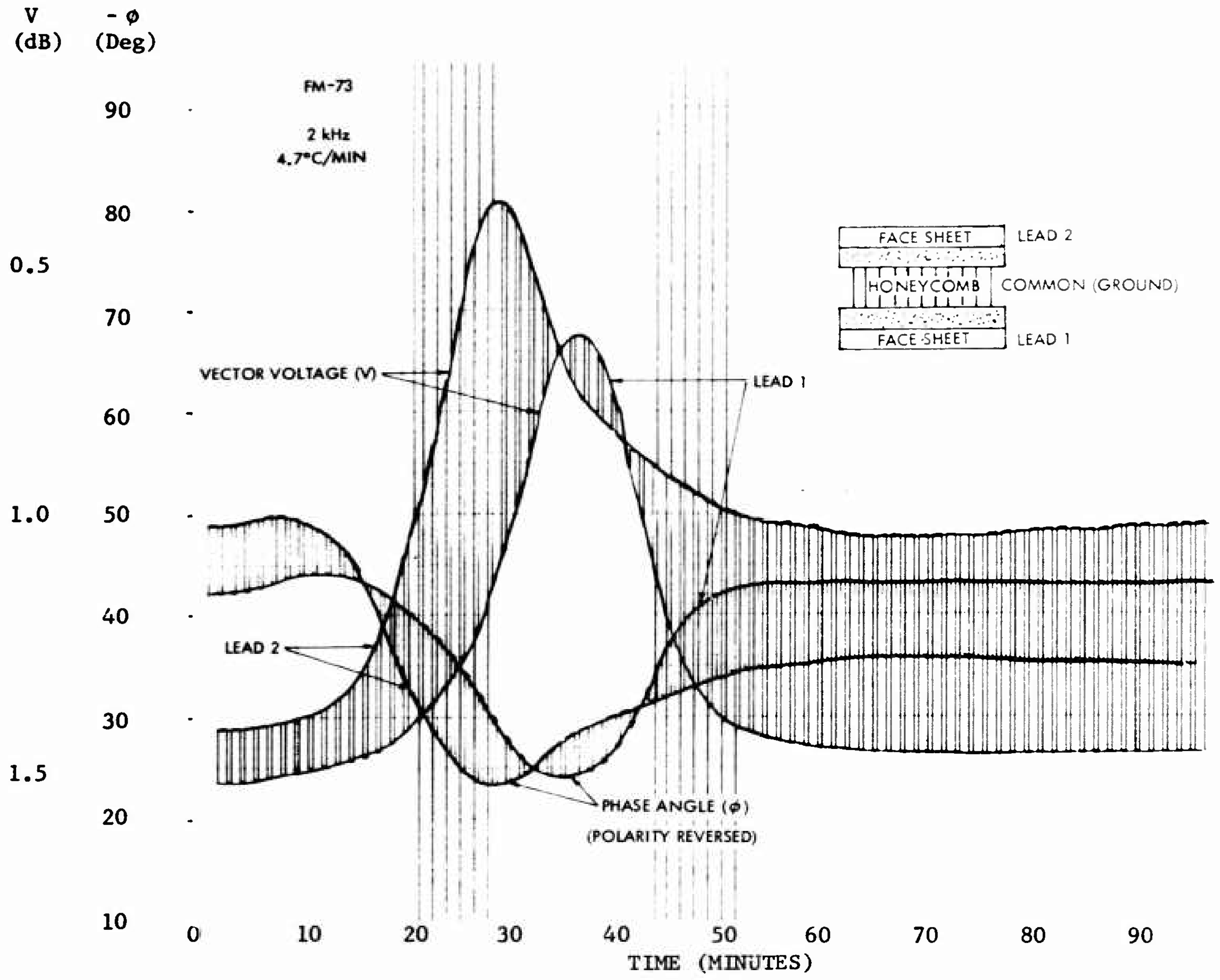


Figure 28. Honeycomb Monitoring Trace 2 kHz

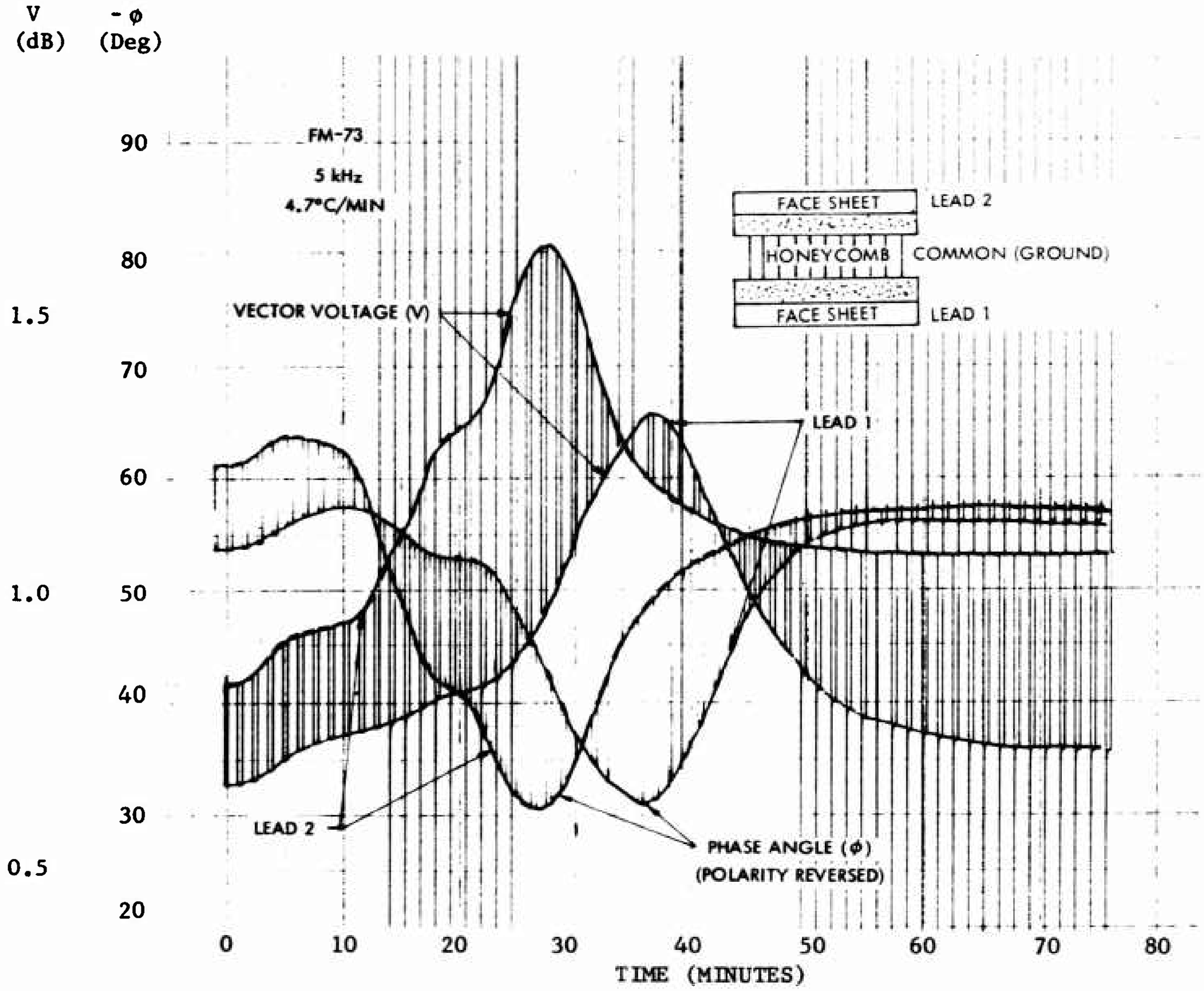


Figure 29. Honeycomb Monitoring Trace 3 kHz

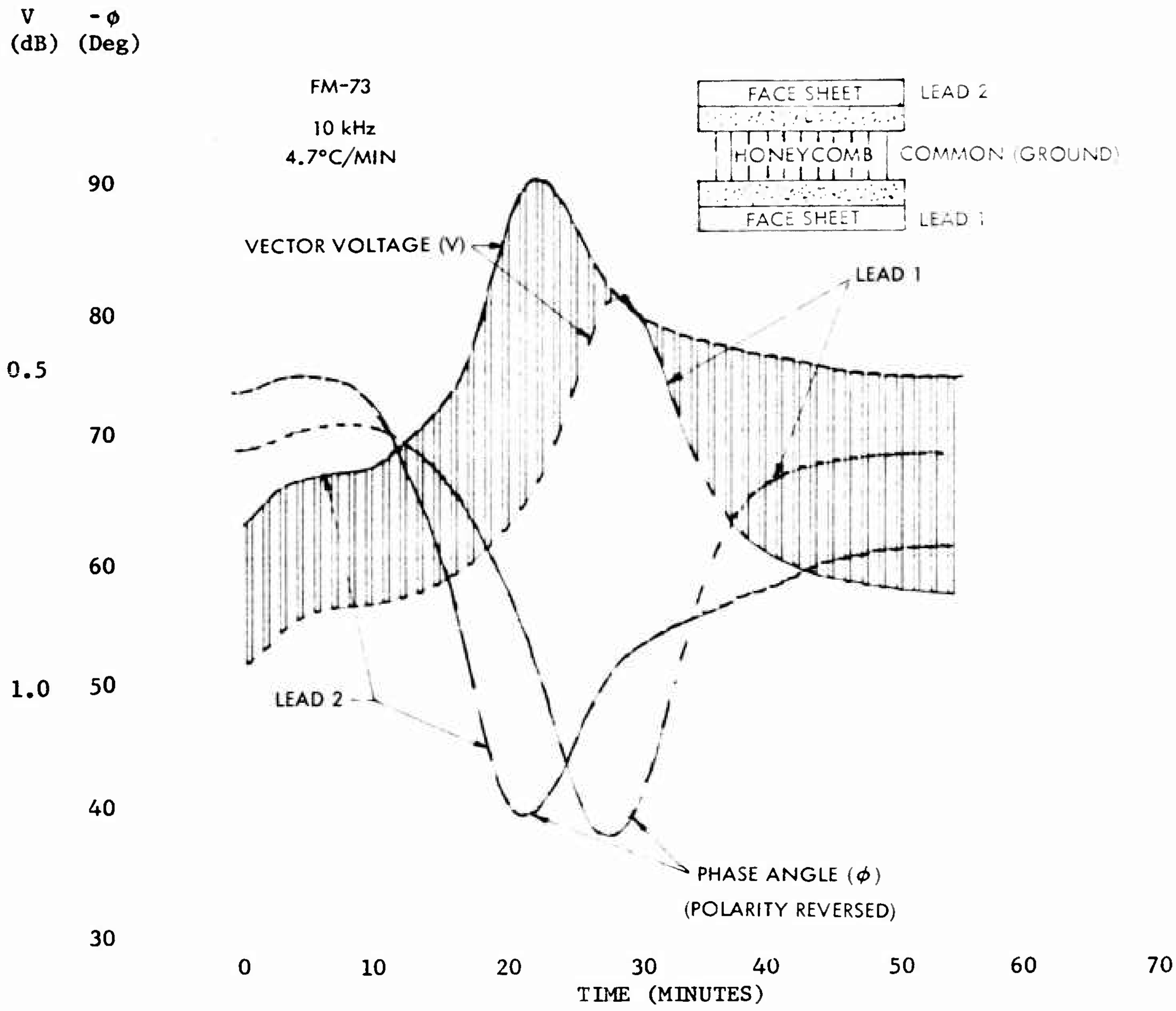


Figure 30. Honeycomb Monitoring Trace 10 kHz

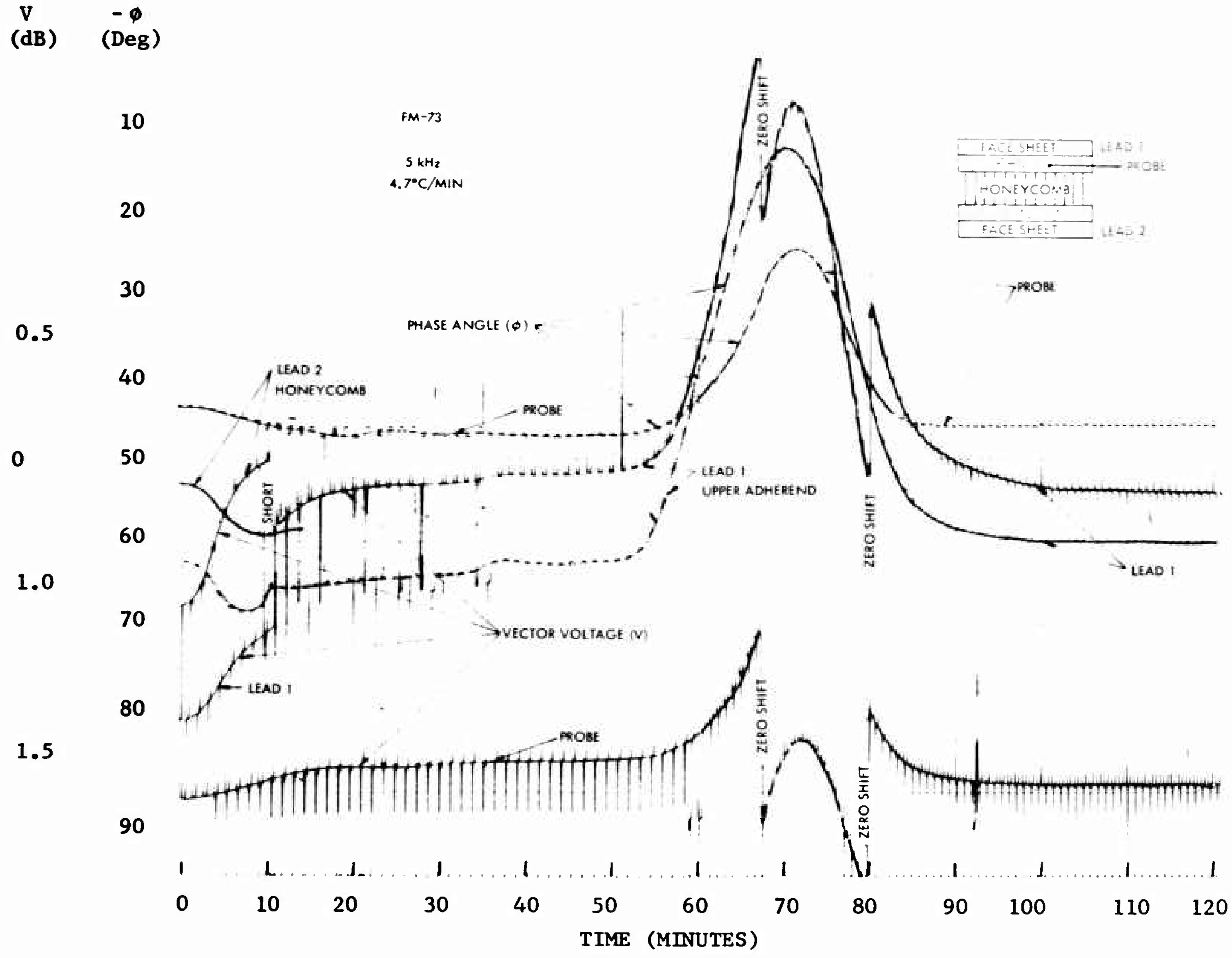


Figure 31. Combined Direct/Internal Approach to Honeycomb Monitoring

III.2.f Cocured Honeycomb

An attempt was made to monitor the cocuring of an aluminum honeycomb, graphite/epoxy prepreg sandwich panels. Although the method, as described below, failed, the importance of this manufacturing technique justifies an extensive investigation.

The method involves using the graphite/epoxy prepreg (Fiberite 934/T300, 24 x 26 8 harness satin cloth) as one of the electrodes and the aluminum honeycomb core (3/16", 44 lb, 5056 Al core) as the other. The monitoring frequency was 5 kHz. The heating rate was 4.7°C (8.6°F) per minute to 177°C (350°F). The adhesive was FM-73 supported on a Dacron mat. Even though several attempts were made, the last in a press at low pressure (ca 5 psi), they all failed due to shorting between the core and the graphite cloth skin.

III.3 Developing the Internal Approach to Adhesive Monitoring

The internal approach to adhesive monitoring, in which a foil probe is embedded directly in the bondline, offers the unique capability of monitoring cure at multiple locations in the same bondline. When used with the phasemeter method of dielectric monitoring the only electrical isolation that is required is for the probe itself. Adherends may be grounded directly to the processing equipment.

Knowing that multiple cure sitescould be monitored, before demonstrating this in the same bondline, the effect of probe geometry on monitoring signal strength and on bond strength were investigated. Finally, eight 45.7 cm (18 inches) wide panels were monitored, cut into lap shear specimens, exposed to various environments and mechanically tested. Monitoring was done in sets of two panels, one with each adhesive, further demonstrating the versatility of the procedure.

III.3.a Influence of Probe Geometry on Monitoring Signal Strength and Lap Shear Bond Strength

Two grades of commercially available aluminum foil were examined for suitability as probes. One grade of "kitchen" foil is 0.018 mm (.0007") thick and a second, the "heavy duty" grade, is 0.031 mm (.0012") thick. It was found experimentally that the thinner foil was more prone to shorting, due to bending and swimming as the adhesive cured. Because of these difficulties, it was decided to use the thicker 0.031 mm (.0012") thick foil.

After deciding on a foil thickness, the next area of concern was the probe width. The influence of probe width on both signal response and mechanical strength were investigated in the following experiments with PL-729. The influence of probe width on signal strength was shown by recording multiplexed signals from probes 1, 2, 3, and 4 mm wide as shown in Figure 32 (Probe Size Response). Although wider probes generally produced higher signals even the narrowest probe gave an acceptable response. The influence of probe width on mechanical strength was determined from lap shear specimens. Results of these tests are shown in Table I and in Figure 33. It appears that: (1) narrower probes lead to higher bond strengths than wider ones, and (2) that probed bonds in general show no serious

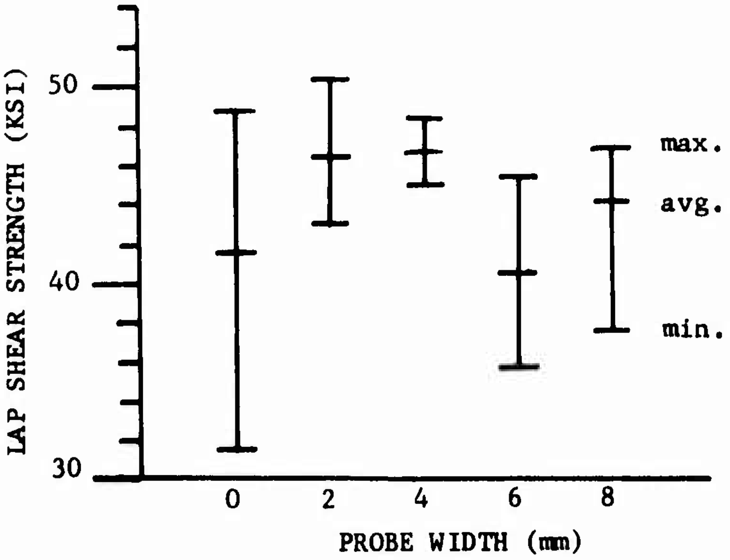


Figure 33. Effect of Probe Width on Lap Shear Strength

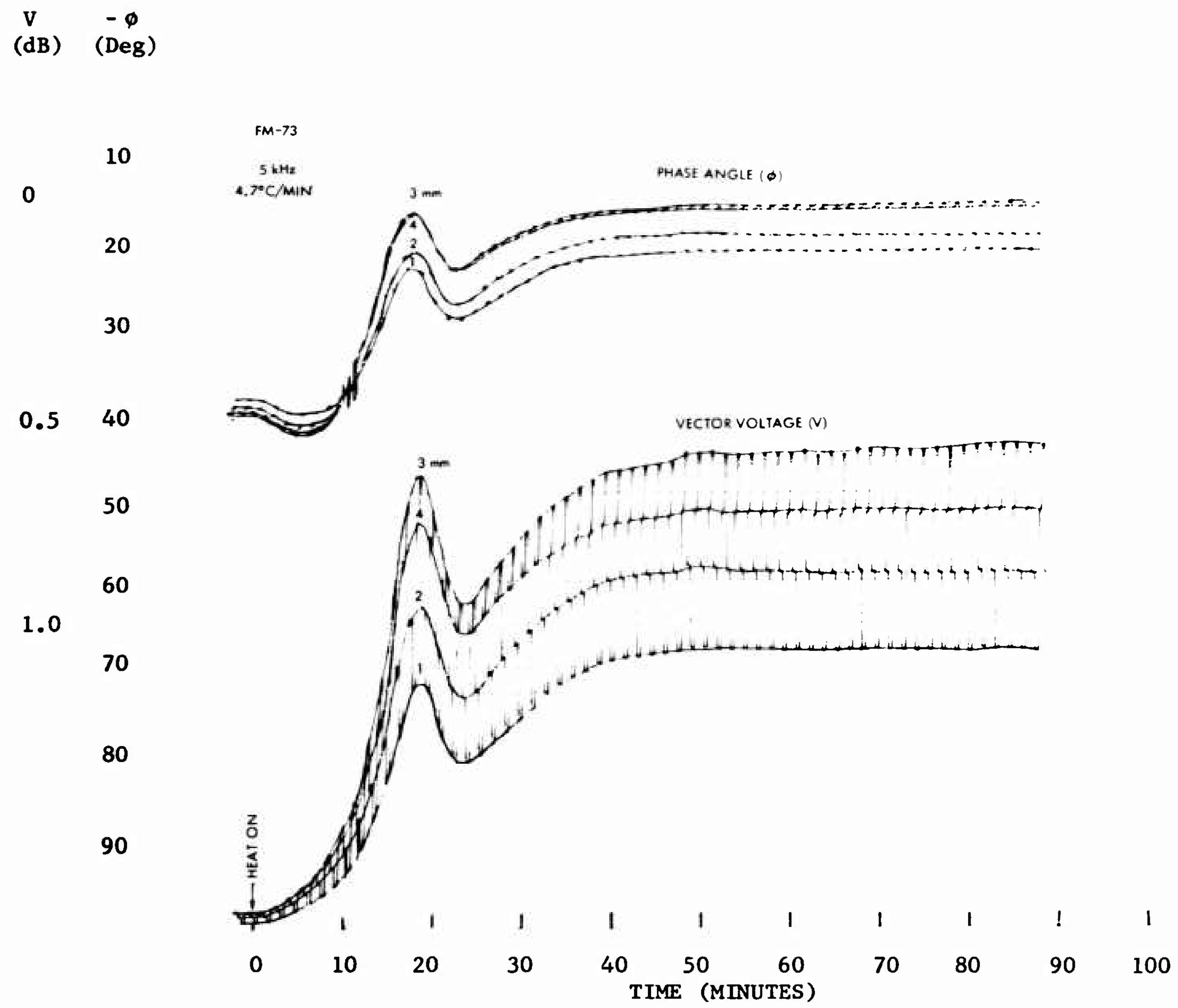


Figure 32. Effect of Probe Width on Signal Strength

TABLE 1

EFFECT OF PROBE WIDTH ON PL-729 BOND STRENGTH

NO PROBE			2mm PROBE			4mm PROBE			8mm PROBE			16 mm PROBE		
SAMPLE NO.	BOND-LINE MILS	PSI	SAMPLE NO.	BOND-LINE MILS	PSI	SAMPLE NO.	BOND-LINE MILS	PSI	SAMPLE NO.	BOND-LINE MILS	PSI	SAMPLE NO.	BOND-LINE MILS	PSI
1	4	4230	2	4	4330	3	4	4520	4	4.3	4510	5	4.4	4810
8	3	4520	6	4.5	4870	7	2.8	4680	9	4.3	4540	10	4.8	4440
17	4.8	4900	11	4.4	4420	12	4.7	4670	13	5.2	4060	14	5.5	4670
18	3.6	4300	15	5.2	4460	16	5	4710	20	4.2	3570	21	4.1	4620
19	2.5	4240	22	2.9	4980	23	4	4480	24	4.2	4400	25	4	4400
26	5	4570	27	4	4680	28	4.3	4810	29	5	3760	30	5.4	4150
35	7.0	3390	31	6	5040	32	6.4	4820	33	7.5	3710	34	7.7	3760
36	7.8	3140												
Average		4161			4682			4670			4078			4407
Average		(28.7 MPa)			(32.3 MPa)			(32.2 MPa)			(28.1 MPa)			(30.4 MPa)

decrease in bond strength. Nonuniform bondline thickness accounts for the high scatter in the baseline bond strengths. Based on these results and physical handling characteristics, 4 mm wide probes were selected for further experimentation.

A photograph of fractured bondlines of both FM-73 and PL-729 adhesives, with and without probes, is shown in Figure 34. Note that the probe fractures uniformly between both adherends.

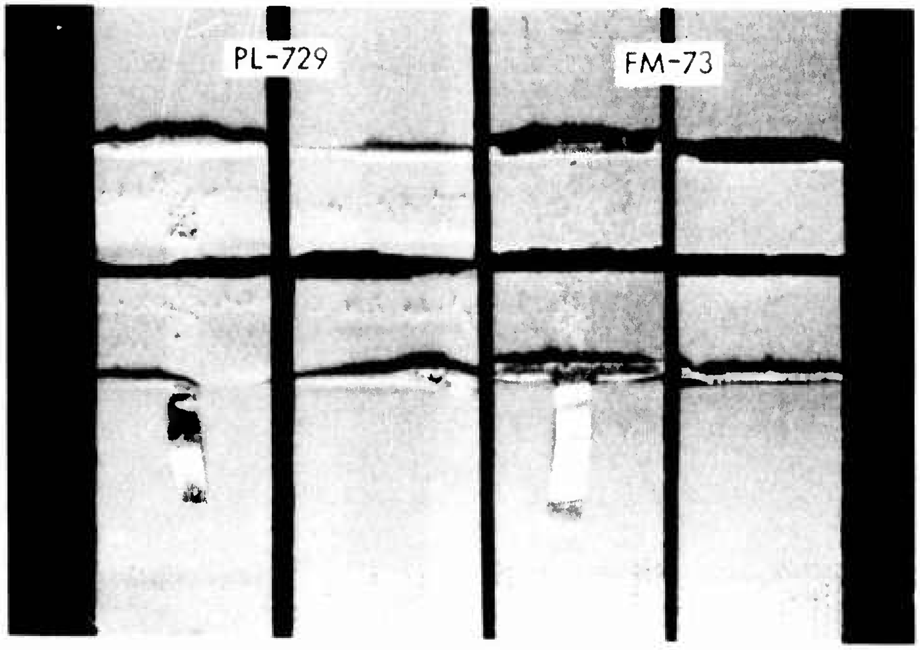


Figure 34. Bondline Fractures

Before leaving the subject of probe width, one additional bit of experimental data should be presented. Half of a 100 mm long bondline containing two layers of FM-73 adhesive was filled with a sheet of primed aluminum foil. After cure, the panel was cut into four 25 mm wide test specimens, two of which contained foil. Strengths of these bondlines are compared to those with only adhesive below:

With Foil	6450, 6250 psi
Adhesive Only	5980, 6050 psi

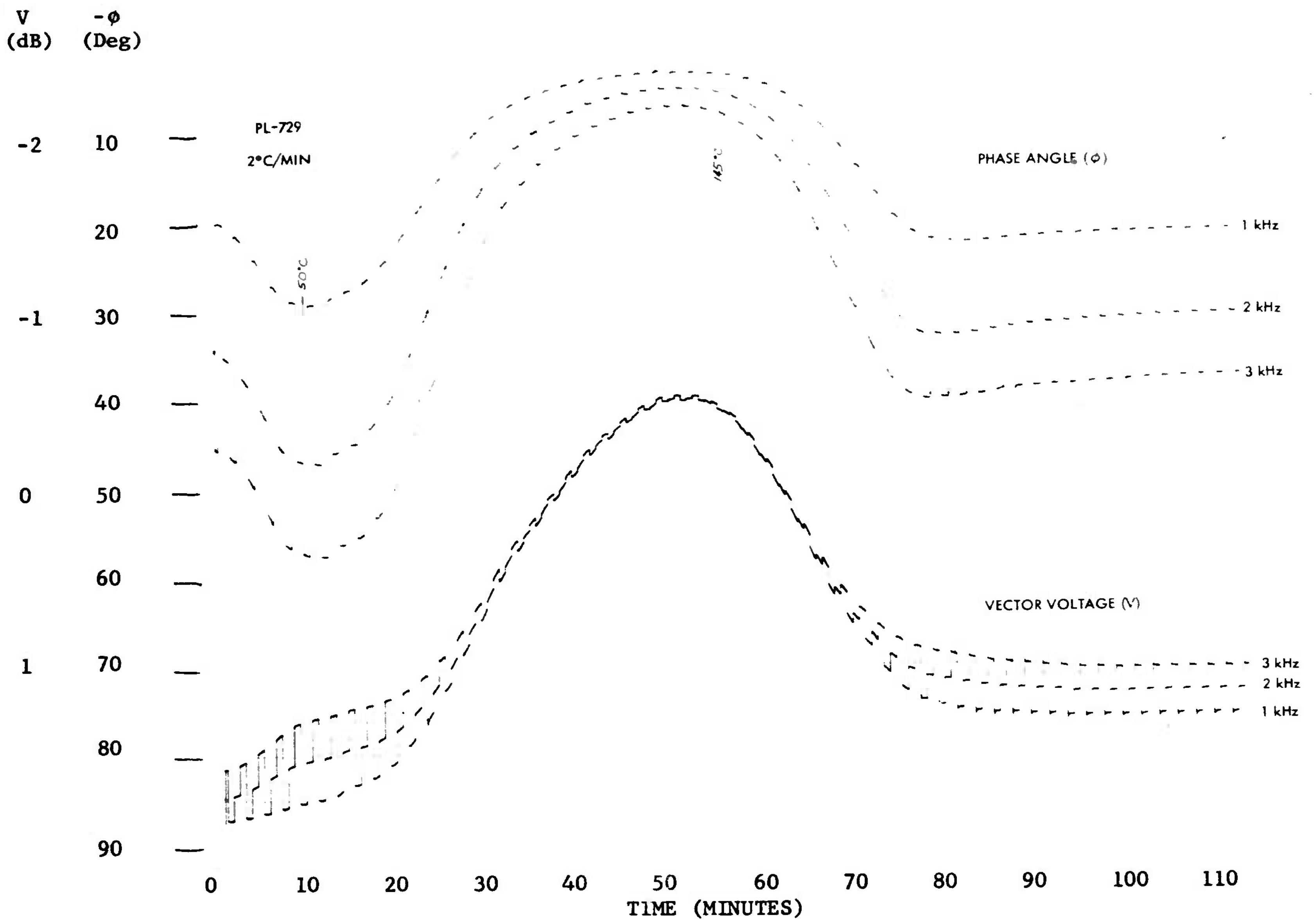


Figure 35. Effect of Frequency on Monitoring Curves

The differences are small (about 8%) and possibly within the range of normal scatter. These experiments suggest that the width of the probe has a minor influence on the measured bond strength.

After scanning at frequencies of 1, 2, and 3 kHz as shown in Figure 35 and finding little effect on signal definition, it was decided that a frequency of 5 kHz which had been used was acceptable.

III.3.b Multipoint Bondline Monitoring

Multipoint bondline monitoring was demonstrated with the internal probing approach using the phasemeter. Both the monitoring configuration and the probe locations in each bondline were discussed in Section II (Figure 13). As a matter of expediency two panels were simultaneously cured and monitored in each of four experimental runs.

The press (75-ton Wabash) used for these cures required more power than the Data Trak could tolerate so that the heating could not be varied. Panel monitoring results are shown in Figures 36, 37, 38, and 39. Corresponding cure schedules may be found in Figure 40, from which initial heating rates of 3.3°C (6°F)/min were determined. Monitoring channels 0, 2, 4, and 6 refer to corresponding positions in PL-729 bondlines and channels 1, 3, 5, and 7-8 to corresponding positions in FM-73 bondlines for all runs except number 2 where the reverse is true. By joining channels 7 and 8 a double time interval conveniently marked the end of each scanning sequence. A sufficient number of channels are labelled in each phase angle trace to identify each adhesive response.

The curves in general are quite reproducible and in excellent agreement with monitoring traces obtained with only one probe per bondline. The cure cycle appears to be adequate as judged by the factor that both phase angle and vector voltage are essentially horizontal after a one hour hold at 177°C (350°F). Good temperature uniformity is indicated by synchronous responses from all probe locations. Note that the departure from the normal heating

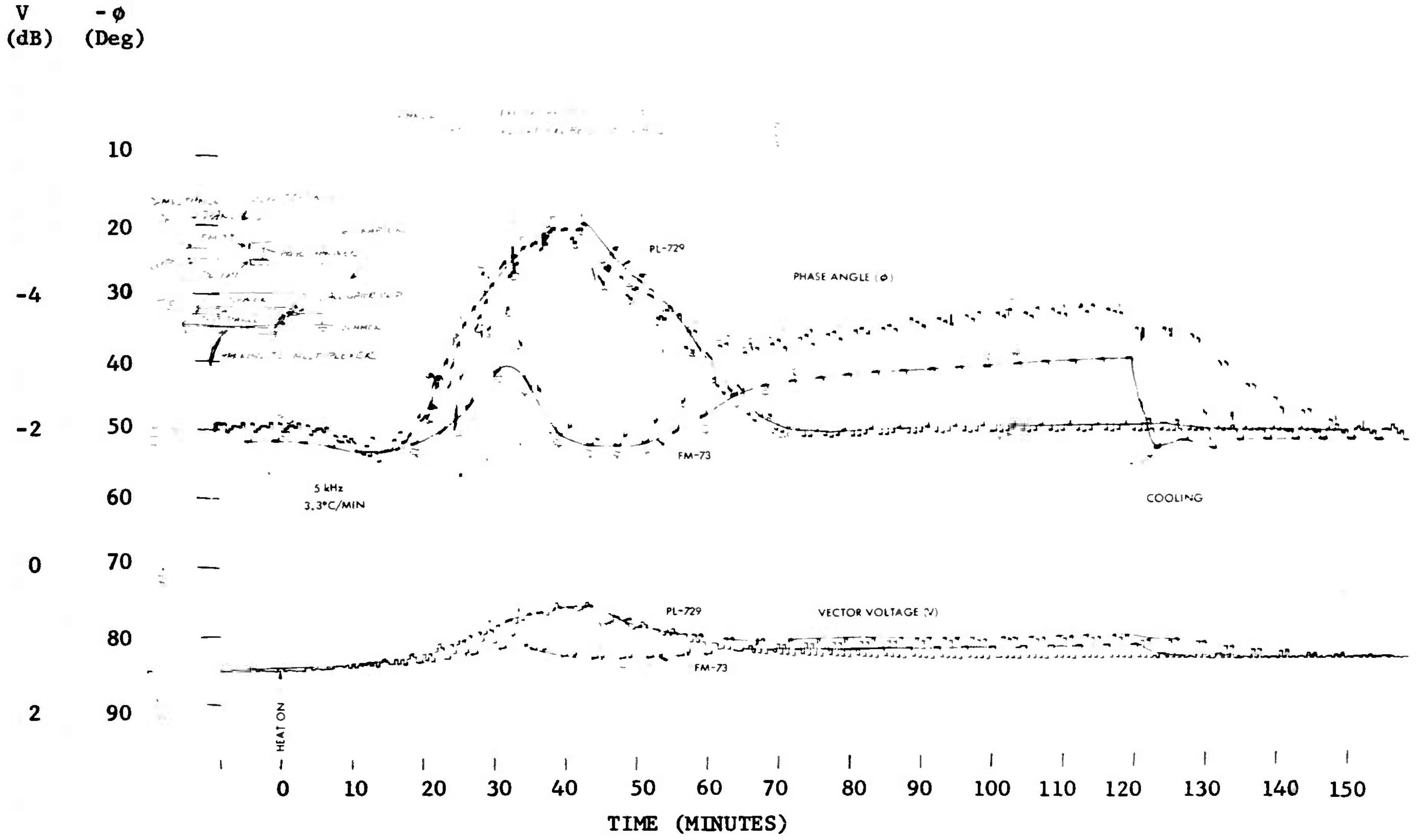


Figure 36. Multipoint Bondline Monitoring Run No. 1

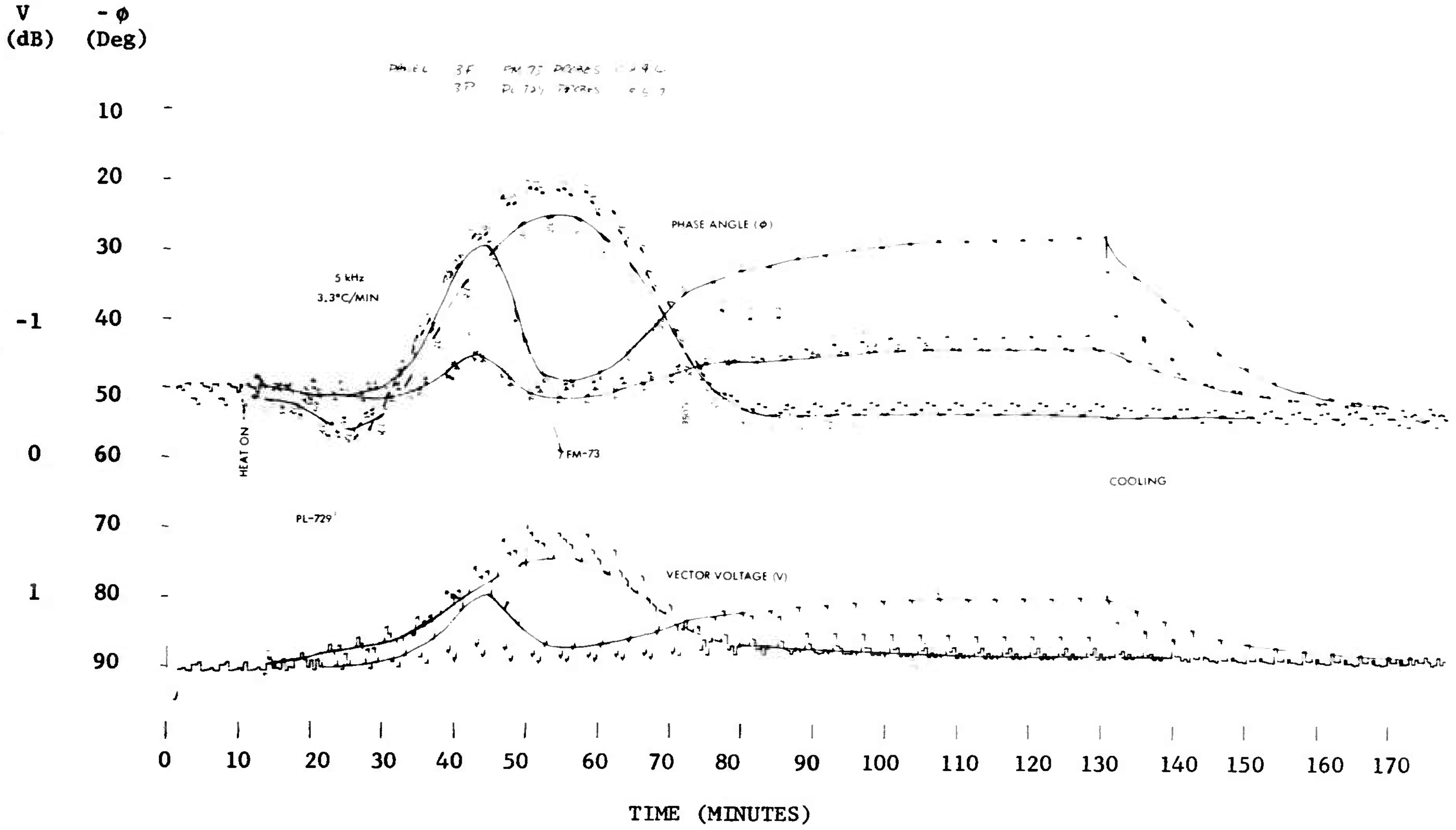


Figure 37. Multipoint Bondline Monitoring Run No. 2

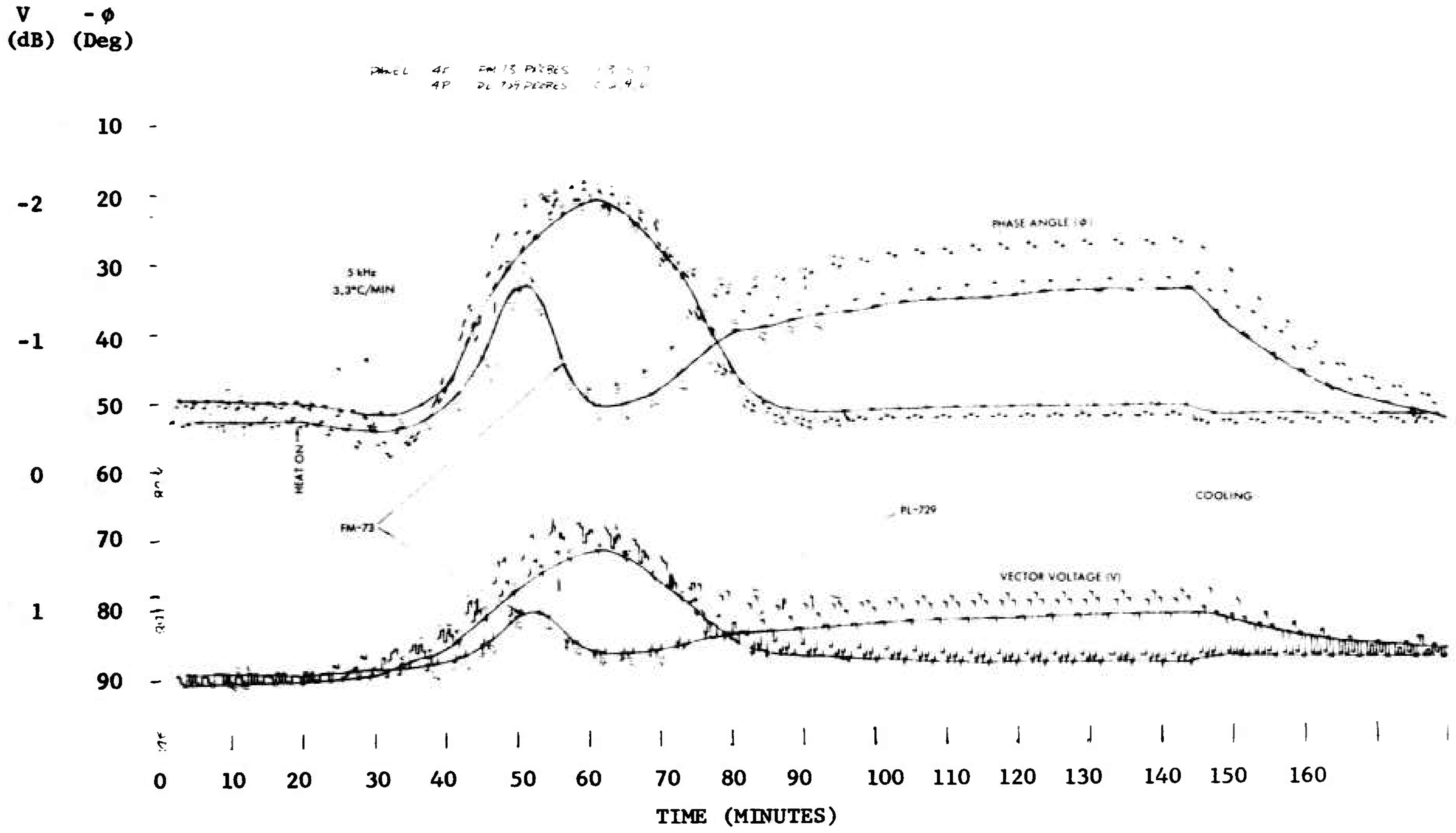


Figure 38. Multipoint Bondline Monitoring Run No. 3

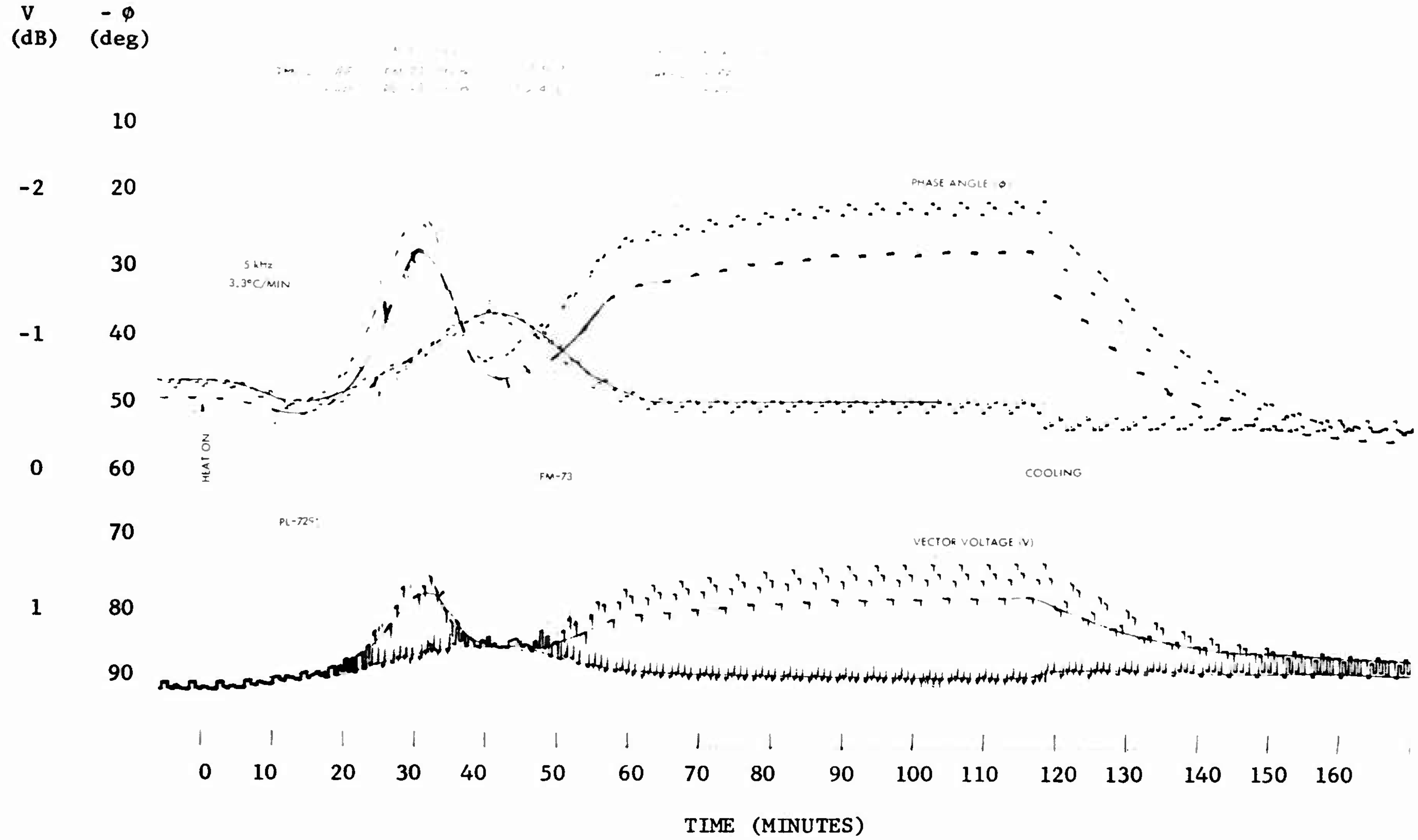
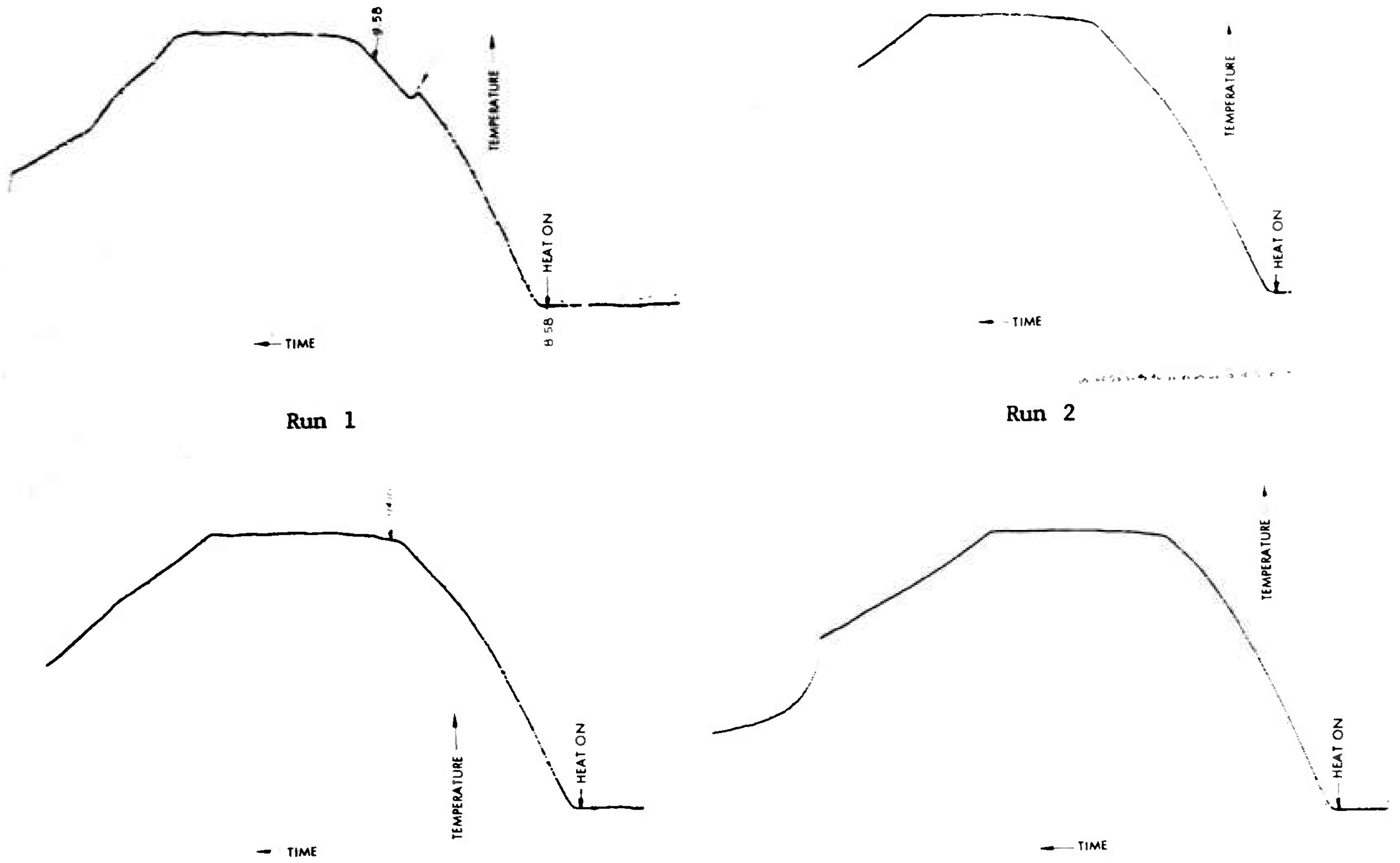


Figure 39. Multipoint Bondline Monitoring Run No. 4



Run 1

Run 2

Run 3

Run 4

Figure 40. Cure Schedules for Run Nos. 1, 2, 3, & 4

rate in Run no. 1 is clearly reflected by the PL-729 response as the adhesive was beginning to cure (see Figures 36 and 40).

A disturbing and puzzling behavior was observed during Runs no. 1 and 3 when several of FM-73 responses became indistinguishable from PL-729 responses. Only the region between 20 and 60 minutes in which a large difference in phase angles occurs between the two adhesives is affected. In all cases the trend is such that the defecting FM-73 probes follow a path of lower phase angle. This leads us to believe that corresponding probes in adjacent bondlines were not adequately isolated from one another. Although it has not been proven, this behavior is regarded as an anomally of this particular experiment in which loose, unmonitored probes were present (see Section II.5). Additional experimentation is required to isolate the origin of this behavior and to verify the soundness of the approach.

A similar monitoring experiment was conducted for a single autoclave run in which aluminum panels were bonded with PL-729. A similar cure cycle was used with the exception that vacuum (720 torr) was maintained throughout the run. Excessive foaming resulted in a very noisy recording. Although characteristic features could be seen the curve was difficult to resolve. It was later realized that vacuum should not be used during the curing of these products.

III.4 Environmental Test Results

Panel to panel variations in bondline thickness found among the panels prepared for environmental testing ranged between 0.08 and 0.39 mm (0.003 and 0.015 inches). Although shimming was incorporated in the monitoring configuration, the precision required for controlling bondline thickness within normal limits, i.e., 0.08 to 0.18 mm (0.003 to 0.007 inches) was not obtained. In order to affect a fair comparison between adhesives in any given environment, similar bondline thicknesses were tested.

Test results are summarized in Tables 2 and 3 where average lap shear strengths for both baseline and exposed specimens as well as average bondline thicknesses are shown. These results are analyzed below. The complete tabulation of test results may be found in Appendix B.

Examination of the baseline data for both adhesives leads to the following observations:

(1) Bondline thicknesses greater than (9.4 mils) lead to reduced bond strengths in the case of FM-73.

(2) Bond strengths for PL-729 are generally lower than those quoted by the vendors, even for thin bondlines.

(3) Probed bondlines are not generally weaker than non-probed ones.

As a generality thinner bondlines give lower strengths in the case of epoxy adhesives. PL-729 bond strengths determined throughout this program were generally low unless slow heating rates 2°C (°F)/min were used. These were obtainable only in the small pneumatic press which had finer temperature control. Lap shear strengths exceeding 5000 psi could be obtained in this manner. The reason may be related to the difference in minimum wetting angle as a function of heating rate as discussed in the following sub-section. The probed bondline strengths were within the normal range of scatter encountered with mechanical testing.

Environmental effects on unprobed bondlines are examined first. Room temperature FM-73 bond strengths are generally diminished after exposure to moisture. The effect is slight (about 10%) following ambient exposure and more serious (20-25%) following exposure to elevated temperatures. These results are in sharp contrast to those found with PL-729 which shows a general increase (20-25%) in RT lap shear strength after moisture exposure.

TABLE 2

PL-729 ENVIRONMENTAL TEST RESULTS

	BASELINE			EXPOSED		
TEST	AVG. BOND-LINE (MILS)	PROBE MPa (KSI)	NO PROBE MPa (KSI)	AVG. BOND-LINE (MILS)	PROBE MPa (KSI)	NO PROBE MPa (KSI)
24 hour water boil	11.9	23.2 (3.4)	21.5 (3.1)	10.9	23.7 (3.4)	26.5 (3.8)
200 hours at 120°F/95% RH	3.2	27.9 (4.1)	30.3 (4.4)	3.1	29.4 (4.3)	30.6 (4.4)
7 day water immersion	14.0	19.0 (2.8)	22.3 (3.2)	15.4	24.8 (3.6)	26.7 (3.9)
30 day water immersion	13.9	24.4 (3.5)	19.3 (2.8)	13.8	30.5 (4.4)	24.2 (3.5)

TABLE 3

FM-73 ENVIRONMENTAL TEST RESULTS

	BASELINE			EXPOSED		
TEST	AVG. BOND-LINE (MILS)	PROBE MPa (KSI)	NO PROBE MPa (KSI)	AVG. BOND-LINE (MILS)	PROBE MPa (KSI)	NO PROBE MPa (KSI)
24 hour water boil	9.3	39.4 (5.7)	34.8 (5.1)	9.2	29.8 (4.3)	31.3 (4.5)
200 hours at 120°F/95% RH	3.9	39.3 (5.7)	43.1 (6.3)	4.0	35.6 (5.2)	38.7 (5.6)
7 days water immersion	13.0	29.7 (4.3)	32.7 (4.7)	11.6	32.0 (4.6)	31.7 (4.6)
30 days water immersion	9.3	39.3 (5.7)	36.4 (5.3)	9.2	37.4 (5.4)	35.6 (5.2)

The only exception to this trend was found for the 200 hr test at 120°F/ 95% R.H. which indicated no significant change due to exposure. These data suggest a more extensive testing program in which strengths at elevated temperatures be determined.

Probed bondlines exhibited the same trends stated above. Little if any detrimental effects could be attributed to probes in the ambient exposures. A slight effect was noted for specimens exposed to moisture at elevated temperatures.

III.5 Neat Resin Characterization

Insight into the rheology of the adhesives during cure and in the glassy state was gained by a few resin characterization techniques. Tensile and flexural properties of resin castings were related to lap shear bond strengths and both dynamic (i.e., programmed heating rates) wetting angle measurements and DSC reaction kinetics were related to dielectric monitoring.

III.5.a Mechanical Properties

Mechanical properties of neat resin castings are shown in Table 4. Tensile modulus and tensile strength are both higher for FM-73 but flexural modulus and flexural strength are the highest for supported PL-729.

Measurements denoted by X and Y were made at 90° to one another so that any anisotrop could be determined. None is apparent. Dacron matte in FM-73 offers little mechanical advantage but the nylon tricot scrim in PL-729 does seem to stiffen this adhesive in both tension and flexural moduli.

TABLE 4

MECHANICAL PROPERTIES OF NEAT RESIN CASTINGS

	PL-729-3 SUPPORTED	PL-729-3 UNSUPPORTED	FM-73 SUPPORTED	FM-73 UNSUPPORTED
Tensile Str., psi	5,095	5,783	X 7,130 Y 7,415	7,363 7,535
Tensile Mod, psi	336,000	304,000	X 367,200 Y 393,700	369,436 348,215
Elongation to Break, %			2.5	3.5
Flex. Str., psi	X 12,911 Y 14,462	9,716 12,400	12,000 11,550	NOT MEASURED
Flex. Mod., psi	X 421,500 Y 420,000	381,500 376,500	370,100 365,400	

The higher tensile modulus of FM-73 influences the shear modulus in the bondline since the two are related by Poisson's ratio, at least for anisotropic elastic materials. The higher tensile strength is significant since high tensile stress concentrations are found at bondline extremities(14). The influence of flexural properties on bond strengths are not evident.

III.5.b Wetting Angle Measurements

Wetting angles were measured for both adhesives at heating rates of 2°C (3.6°F)/min and 5°C (9°F)/min. The results are shown in Figure 41 on properly primed FPL etched surfaces. Stepped decreases in wetting angle, which are more apparent for PL-729, reflect the thixotopic action of the fillers. Better wetting is generally found at the lower heating rates. Minimum wetting angles for FM-73 are consistently lower than those for PL-729. The difference in minimum wetting angles for PL-729 at each heating

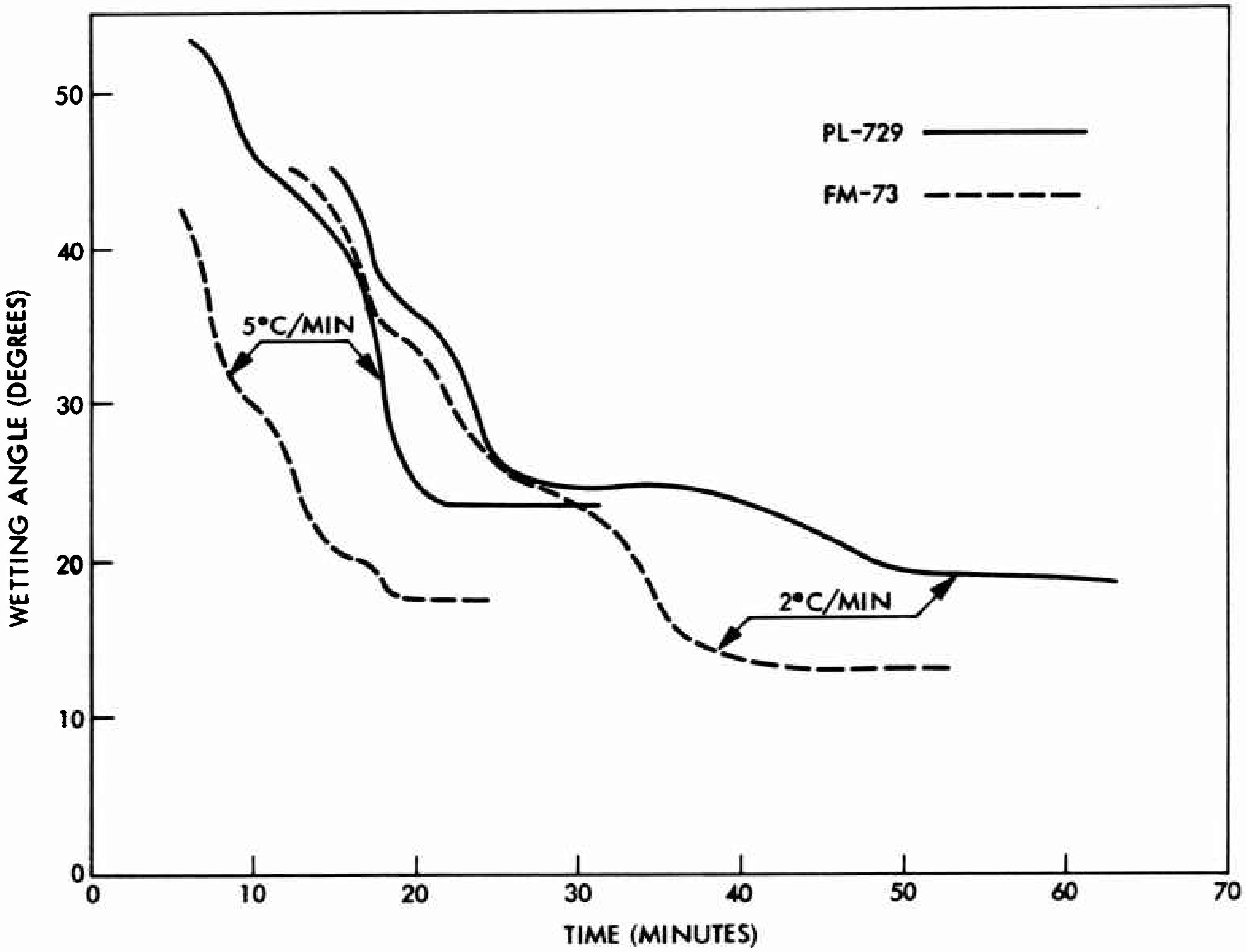


Figure 41. Dynamic Wetting Angle Measurements

rate may account for the lower bond strengths measured on specimens cured at faster heating rates. Dynamic wetting angle measurements are a valuable technique for optimizing cure cycles.

III.5.c Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) results are shown in Figures 42, 43, 44, and 45 where PL-729 and FM-73 were scanned at 2°C (3.6°F)/min. and 5°C (9°F)/min. using two levels of sensitivity.

The effect of heating rate on PL-729 reaction kinetics is shown by comparison of Figures 42 and 43. The faster heating rate shifts the peak exotherm from 174°C (345°F) to 194°C (384°F). Below ambient scans indicate a T_g of about 0-3°C for the uncured adhesive. Findings of a related research program at LMSC indicate that changes in the T_g of an uncured resin may be related to the extent of B-staging. After a one hour hold at 177°C (350°F) in the DSC, no T_g could be found during a slow cool down to 75°C (167°F), thus indicating a T_g of at least 177°C (350°F).

The effect of heating rate on FM-73 reaction kinetics is shown by comparison of Figures 44 and 45. Note that in these curves the temperature was scanned to 177°C (350°F) and held as opposed to the previous curves where temperatures were scanned directly to 194°C (384°F). Had the PL-729 been held at the 177°C (350°F) cure temperature, the change in location of the peak exotherm would have been obscured since it cures at a slower rate. The higher heating rate shifts the peak exotherm from 130°C (266°F) to 143°C (290°F) but has little influence on the onset of cure. Exotherms displayed upon reaching the hold temperature are instrumental artifacts which should be ignored. The ensuing portion of each curve should be shifted downward to smoothly continue with the first.

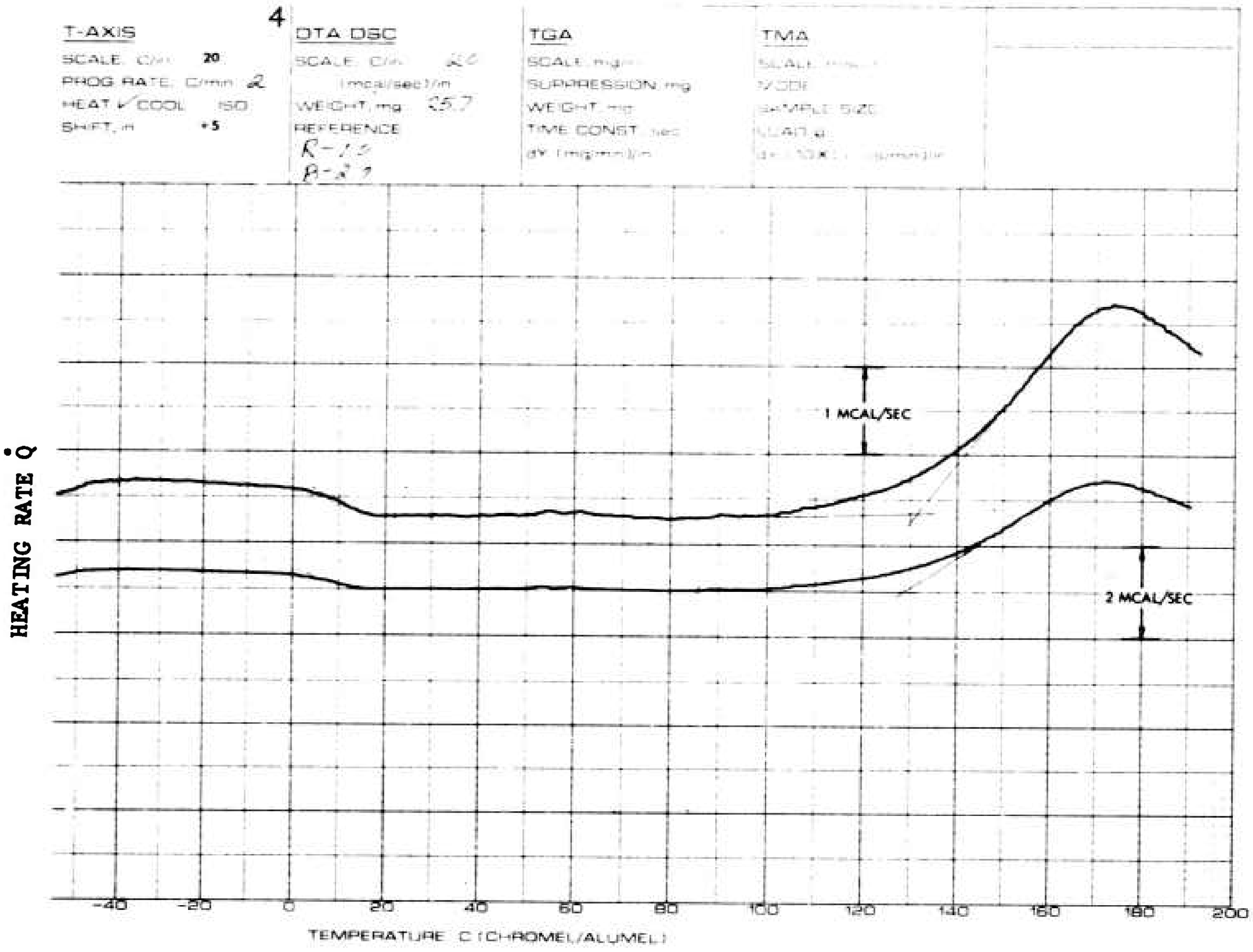
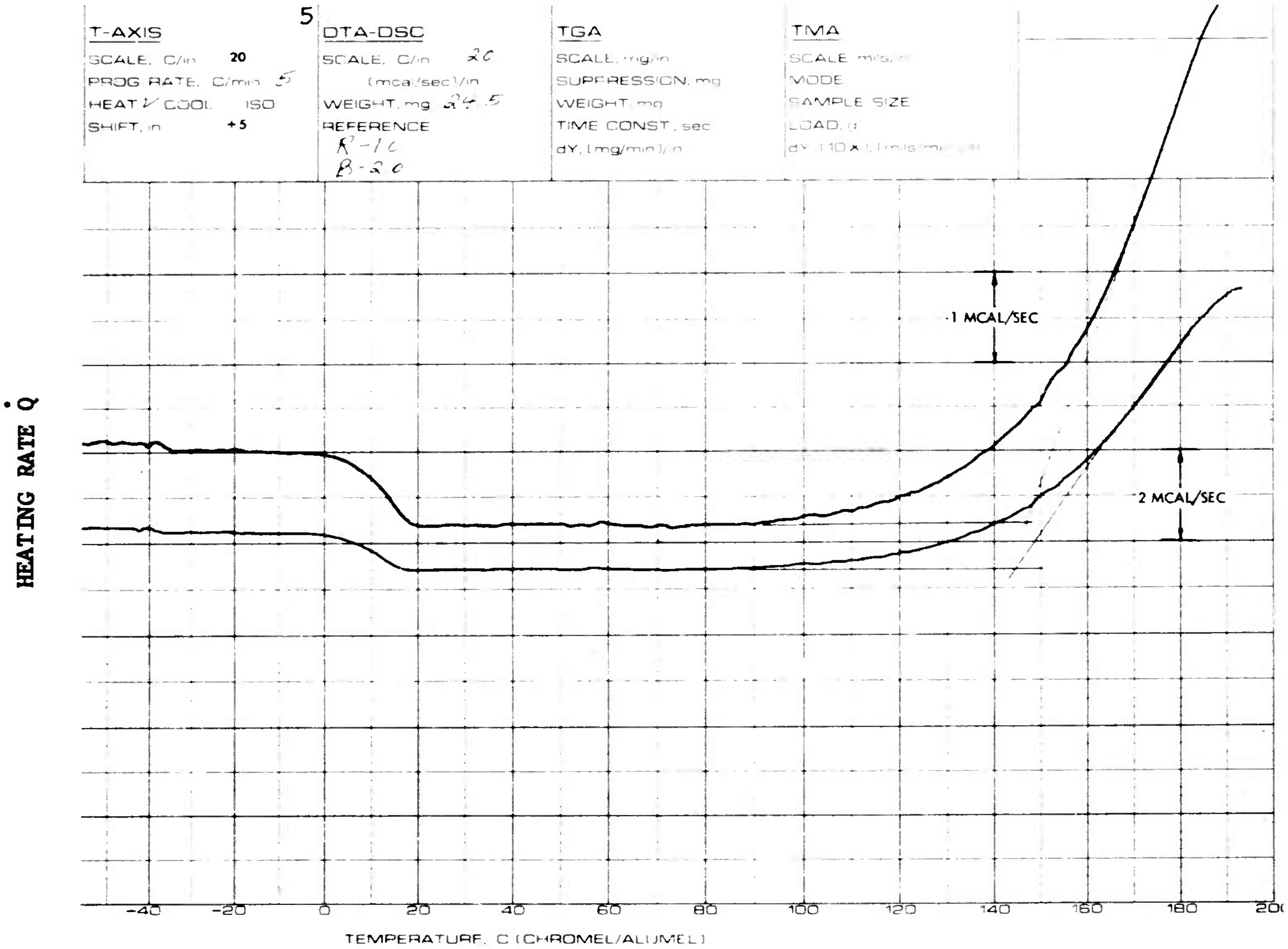


Figure 42. DSC Curve - PL-729 at 2°C/Min.



T-AXIS
SCALE, C/in 20
PROG RATE, C/min 5
HEAT ✓ COOL ISO
SHIFT, in +5

5

DTA-DSC
SCALE, C/in 20
(mcal/sec)/in
WEIGHT, mg 24.5
REFERENCE
R-10
B-20

TGA
SCALE, mg/in
SUPPRESSION, mg
WEIGHT, mg
TIME CONST, sec
dY, (mg/min)/in

TMA
SCALE mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10 x) (mils/min)/in

Figure 43. DSC Curve - PL-729 at 5°C/Min.

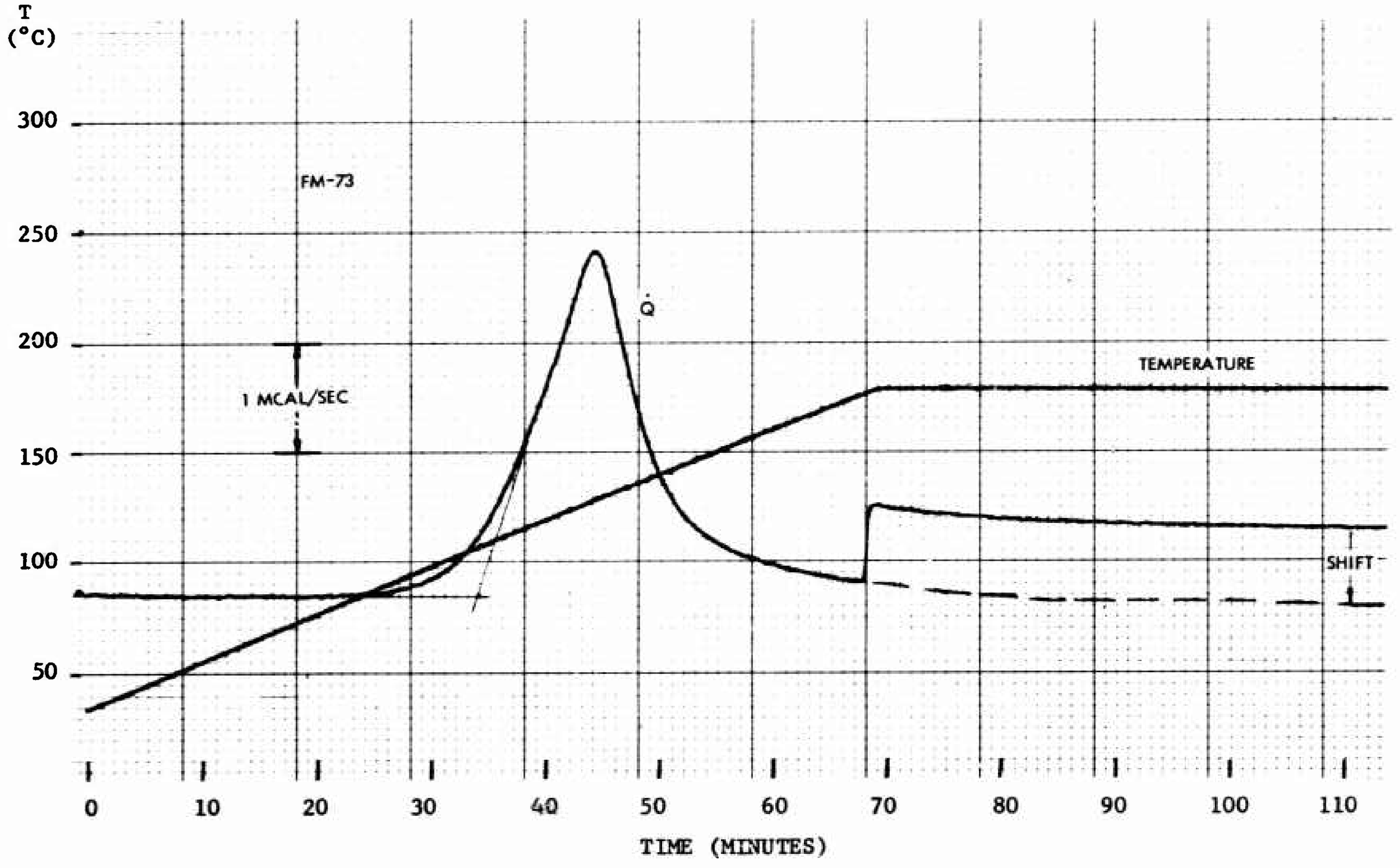


Figure 44. DSC Curve - FM-73 at 2°C/Min.

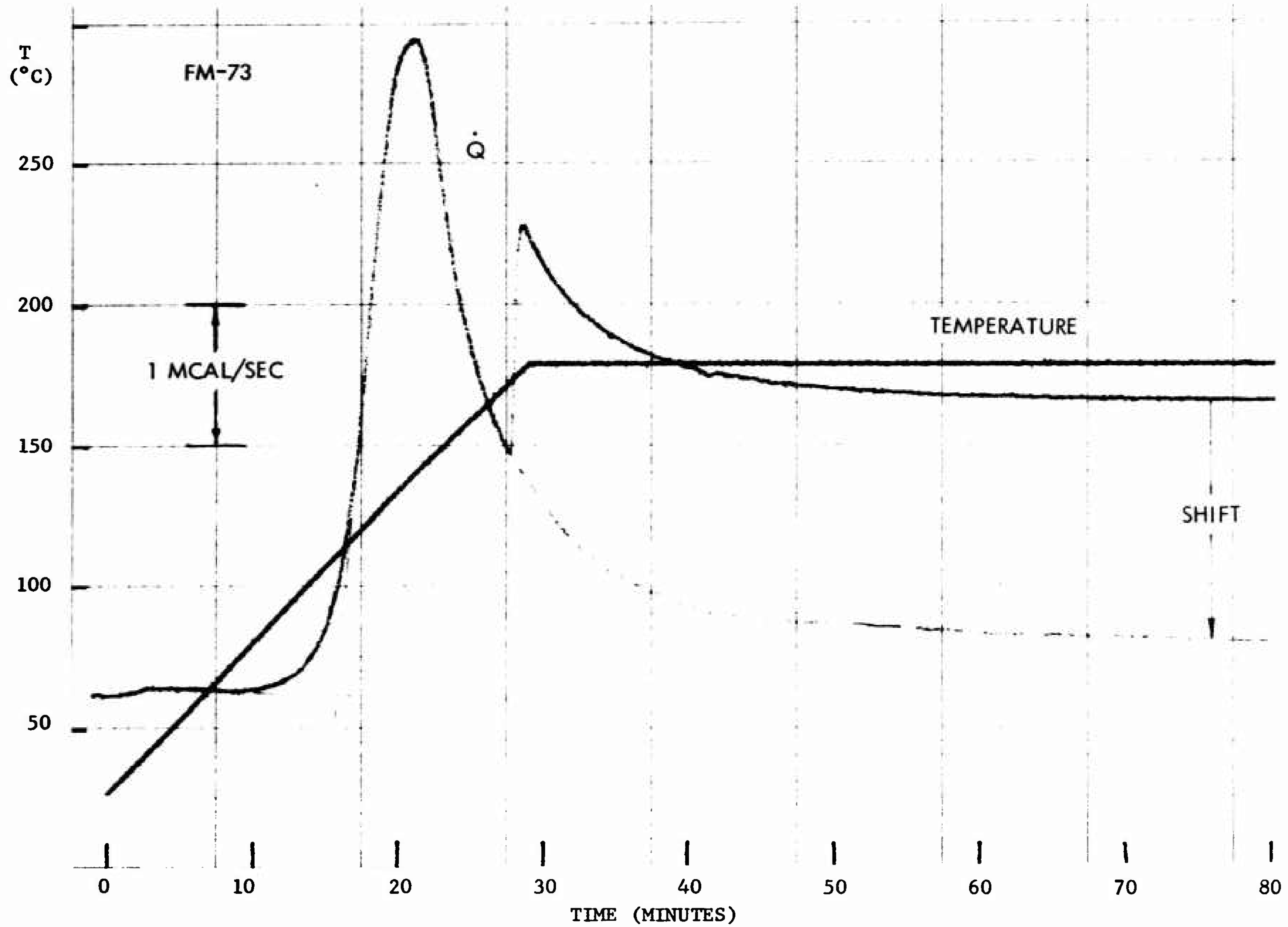


Figure 45. DSC Curve - FM-73 at 5°C/Min.

III.5.d Correlations With Dielectric Monitoring

Dynamic wetting angles measurements and DSC reaction kinetics were correlated with dielectric monitoring curves for PL-729 at the same heating rate as shown in Figure 46. Softening and cure related peaks in both Audrey and phasemeter traces reflect these changes quite well. The valley between peaks represents a region where further reductions of wetting angles are limited by the onset of cure. The initial rise of the cure related peak occurs after the onset of cure, and closer to the gel point than the initial decay of the single iongraphing peak. The results clearly indicate that heating rates are a critical factor in the bonding process.

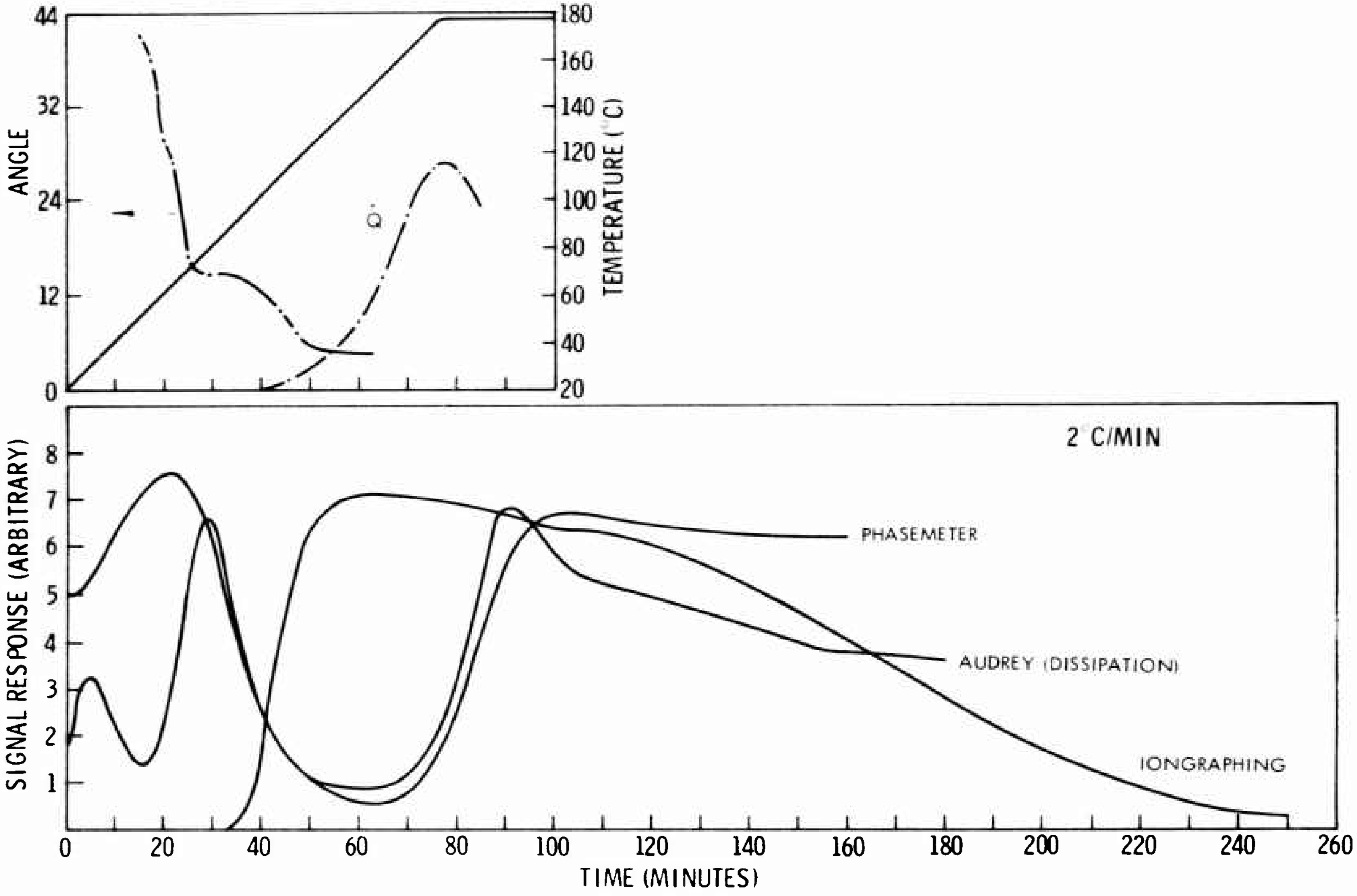


Figure 46. Correlation of Wetting Angle Measurements and Reaction Kinetics With Dielectric Monitoring Traces

Section IV

CONCLUSIONS

Dielectric monitoring methods in general are useful for following cure in adhesive bondlines. The phasemeter method provides the most active approach for production applications because it offers more information than iongraphing and has a higher signal-to-noise ratio than the Audrey. The internal probing technique developed in this program offers the distinct advantage of following cure rates in selected portions of a bondline. When coupled with the phasemeter this approach requires minimal electrical isolation. The effect of an imbedded probe in a bondline on room temperature lap shear strengths was shown to be minimal even after environmental exposure. Environmental testing resulted in decreased room temperature bond strengths for FM-73 but increased bond strengths for PL-729.

Physical characterization of the adhesives by dynamic wetting angle measurements and DSC was a valuable complement to the monitoring effort. FM-73 was found to wet a properly primed aluminum substrate better than PL-729 regardless of the heating rate used. These differences probably reflect formulation variables and possibly degree of B-staging. The differential scanning calorimetry data shows that FM-73 cures at a faster rate than PL-729. This is not unexpected since PL-729 has an aromatic amine curing agent as compared to what is probably an accelerated dicyandiamide cure in the case of FM-73. This data also indicates that PL-729 must be cured at 177°C (350°F) minimum to obtain complete cure with a reasonable processing time. One can also question whether or not all of the epoxide has been reacted in this product since the dielectric data indicates the glass transition temperature is greater than 177°C (350°F). Additional mechanical property measurements are needed before a meaningful correlation with bond strength can be made.

Section V

RECOMMENDATIONS

The following recommendations are made as a result of this investigation.

- Continue to explore the effects of imbedded foil probes by generating statistically significant mechanical data, by testing bondlines at elevated temperatures and by examining the long term effects on bond integrity.
- Develop the external probing method for non-conductive adherends.
- Apply the phasemeter method to limited production applications.
- Test environmentally exposed specimens at elevated temperatures.
- Monitor cure of additional adhesive systems.
- Investigate metal powder filled adhesives.
- Develop correlations between the neat adhesive mechanical and physical properties and bond performance with particular attention to the effect of heating rate.

APPENDIX

1 Cleaning and Etching Procedures

1.a FPL Etch

1. Wipe sample with M.E.K. (Methyl Ethyl Ketone).
2. Air dry, room temperature.
3. Alkaline clean, 6-8 minutes, 170°-195°F (76°-90°C),
   Alkalume 13 6-8 oz/gal (44-60 gm/l).
4. Rinse in tap water minimum of 3 minutes.
5. Etch 10-12 minutes, 145°-155°F (63°-69°C),

3.5-4.3 oz/gal (26.2-32.2 gm/l)	Sodium Dichromate $Na_2Cr_2O_7 \cdot 2H_2O$
20 25 fl. oz/gal (150-186 ml/l)	Sulfuric Acid H_2SO_4

6. Deionized water rinse, minimum 3 minutes.
7. Air dry, room temperature.

1.b Titanium Surface Preparation

1. Solvent wipe using methyl ethyl ketone (MEK).
2. Alakline clean using Kelite 236, 8 to 16 ounces/gallon (oz/gal) concentration, or equivalent, at 140° to 180°F for 5 to 15 minutes.
3. Immerse or spray rinse using room temperature tap water and check for a water-break-free surface[b].

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[b] 50 ppm solids max.; 30 ppm chlorides max.; pH 4.0-7.0.

4. Pickle for 30 to 60 seconds in an aqueous solution maintained at room temperature as follows:

(Nitric Acid)	HNO_3 (70%)	36 to 50 fluid oz/gal.
(Hydrofluoric Acid)	HF (48%)	5.0 to 7.5 fluid oz/gal.

5. Immerse or spray rinse using room temperature deionized water[a,b].
6. Immerse for 2 to 3 minutes in an aqueous solution maintained at room temperature as follows:

(Trisodium Phosphate)	$Na_3PO_4 12\ H_2O$	6.0 to 7.6 oz/gal.
(Potassium Fluoride)	$KF.2H_2O$	2.4 to 3.0 oz/gal.
(Hydrofluoric Acid)	HF (48%)	3.8 to 5.0 fl. oz/gal.

7. Spray rinse in room temperature deionized water for 2 minutes, minimum.
8. Immersion soak in unagitated deionized water for 15 to 20 minutes at 160 ± 15°F and check for a water-break-free surface[b].

   If water-break is obtained, repeat steps 2 through 8.
9. Dry 30 minutes minimum at 140 ± 10°F.
10. If stored for more than 4 hours prior to priming, repeat steps 6 through 9. If not primed immediately, the detail must be wrapped in Kraft paper and protected from contamination as required by Facilities Control until ready for priming. All handling of cleaned details must be performed with clean, lint-free, white gloves.

2. Environmental Test Data

The following tables (A-1 through A-4) contain tabulated results for FM-73 and PL-729 lap shear specimens both before and after exposure to be indicated environmentals. Bondline thicknesses were measured prior to exposure.

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[a] Use demineralized or deionized water for all applications of steps 5 through 8.

[b] 50 ppm solids max.; 30 ppm chlorides max.; pH 4.0-7.0.

TABLE A-1

FM-73 ENVIRONMENTAL TEST RESULTS

7 DAY WATER IMMERSION						30 DAY WATER IMMERSION					
SAMPLE NO. BASELINE	EXPOSED	BONDLINE THICKNESS (MILS)		BASELINE STRENGTH (PSI)	EXPOSED STRENGTH (PSI)	SAMPLE NO. BASELINE	EXPOSED	BONDLINE THICKNESS (MILS)		BASELINE STRENGTH (PSI)	EXPOSED STRENGTH (PSI)
4FON	4F1N	10	9	5590	5260	3FON	3F1N	7	7	5470	5730
4N	2N	12.5	10	4350	4980	4N	2N	9	8	5540	5610
7N	3N	15	11	4370	4850	7N	3N	10	9	5180	5350
8	5N	16	13	4660	4036	8	5N	12	11	4920	4220
	6N		14		3880		6N		11		4920
4FOP	4F1P	9.5	9	4450	5070	4FOP	3F1P	6	7	5650	5650
4P	2P	13	10	3230	5500	4P	2P	10	8	5470	5640
7P	3P	15	12	5250	5290	7P	3P	11	9	6000	5610
	5P		14		3380		5P		11		5060
	6P		14		3980		6P		11		5160
<u>Average</u>											
No Probe				4742 (32.7 MPa)	4600 (31.7 MPa)					5277 (36.4 MPa)	5166 (35.6 MPa)
Probe				4310 (29.7 MPa)	4644 (32.0 MPa)					5706 (39.3 MPa)	5424 (37.4 MPa)

TABLE A-2

FM-73 ENVIRONMENTAL TEST RESULTS

24 HR WATER BOIL						200 HRS 95% R.H. 120°F					
SAMPLE NO. BASELINE	EXPOSED	BONDLINE THICKNESS (MILS)		BASELINE STRENGTH (PSI)	EXPOSED STRENGTH (PSI)	SAMPLE NO. BASELINE	EXPOSED	BONDLINE THICKNESS (MILS)		BASELINE STRENGTH (PSI)	EXPOSED STRENGTH (PSI)
5AF0N	5AF1N	12	11	5090	4520	5BF0N	5BF1N	3	3.5	6420	5260
4N	2N	8	10	4950	4310	4N	2N	4	4	6350	5510
7N	3N	9.5	8	4700	4620	7N	3N	4	4	6530	5600
8	5N	8	8.5	5470	4630	8	5N	4	4	5710	5840
	6N		9		4620		6N		4		5860
5AF0P	5AF1P	11	10	2980	3500	5BF0P	5BF1P	4	4	5110	5140
4P	2P	8	10	5670	4590	4P	2P	4.5	4	5950	4740
7P	3P	9.5	8	5750	4680	7P	3P	4.0	4	6040	5940
	5P		8.5		4480		5P		4		5140
	6P		9		4380		6P		4		4880
Average											
No Probe				5052 (34.8 MPa)	4540 (31.3 MPa)					6252 (43.1 MPa)	5614 (38.7 MPa)
Probe				5710 (39.4 MPa)	4326 (29.8 MPa)					5700 (39.3 MPa)	5168 (35.6 MPa)

TABLE A-3

PL-729 ENVIRONMENTAL TEST RESULTS

7 DAY WATER IMMERSION						30 DAY WATER IMMERSION					
SAMPLE NO. BASELINE	EXPOSED	BONDLINE THICKNESS (MILS)		BASELINE STRENGTH (PSI)	EXPOSED STRENGTH (PSI)	SAMPLE NO. BASELINE	EXPOSED	BONDLINE THICKNESS (MILS)		BASELINE STRENGTH (PSI)	EXPOSED STRENGTH (PSI)
2PON	2P1N	13	15.5	3230	3830	4PON	4P1N	10	12	4246	4120
4N	2N	15	14	2830	3530	4N	2N	14	13	2510	3690
7N	3N	16	15	3150	3970	7N	3N	16	14	2190	3440
8	5N	14	17	3710	4060	8	5N	17	14	2240	3040
	6N		16		3940		6N		15		3250
2POP	2P1P	15	15	2720	4190	4P1P	4P1P	11	13	3510	4800
4P	2P	16	14	2640	3570	4P	2P	13.5	13	3670	4160
7P	3P	15	16	2890	3440	7P	3P	15.5	14	3420	4540
	5P		16		3510		5P		14.5		4150
	6P		15		3250		6P		15		4480
Averages											
Without Probe				3230 (22.3 MPa)	3866 (26.7 MPa)					2795 (19.3 MPa)	3508 (24.2 MPa)
With Probe				2750 (19.0 MPa)	3592 (24.8 MPa)					3533 (24.4 MPa)	4426 (30.5 MPa)

TABLE A-4

PL-729 ENVIRONMENTAL TEST RESULTS

24 HR WATER BOIL						200 HRS 95% R.H. 120°F					
SAMPLE NO. BASELINE	EXPOSED	BONDLINE THICKNESS (MILS)		BASELINE STRENGTH (PSI)	EXPOSED STRENGTH (PSI)	SAMPLE NO. BASELINE	EXPOSED	BONDLINE THICKNESS (MILS)		BASELINE STRENGTH (PSI)	EXPOSED STRENGTH (PSI)
3PON	3P1N	7	9	3580	4080	5BPON	5BP1N	3	3	4230	4400
4N	2N	11	10	3250	3840	4N	2N	3	3	4440	4560
7N	3N	15	11	2750	3740	7N	3N	4	3	4780	4900
8	5N	15.5	11	2870	3790	8	5N	3	3	4130	4270
	6N		13		3800		6N		3.5		4050
3POP	3P1P	8.5	9.5	3710	3320	5BPOP	1P	3	3	4180	4200
4P	2P	10.5	10	3540	3310	4P	2P	3	3	4070	4170
7P	3P	16	11	2830	3050	7P	3P	3.5	3	3910	4310
	6P		14		3920		6P		3.5		4390
Average											
No Probe				3112 (21.5 MPa)	3850 (26.5 MPa)					4395 (30.3 MPa)	4436 (30.6 MPa)
Probe				3360 (23.2 MPa)	3432 (23.7 MPa)					4053 (27.9 MPa)	4258 (29.4 MPa)

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