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DEVELOPMENT OF TEST METHODOLOGY FOR DYNAMIC MECHANICAL ANALYSIS INSTRUMENTATION

Prepared by:	Vernon R. Allen, Ph. D.
Academic Rank:	Professor
University and Department:	Tennessee Technological University Department of Chemistry
NASA/MSFC	
Division:	Non-Metallic Materials
Branch:	Polymers and Composites
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Vernon R. Allen, Ph.D.
Professor of Chemistry
Tennessee Technological University
Cookeville, Tennessee

ABSTRACT

The high technology requirements for deep-space exploration, for extended periods in near-space, and for an over-riding need for energy conservation demand the development of new materials and for controlled variability of the engineering properties of these materials.

Dynamic mechanical analysis is the study of the mechanical properties, e.g. dynamic tensile storage modulus and energy damping, which define the stiffness and the mechanical energy dissipation (as heat) of the sample under sinusoidal stress. This project was designed to utilize the "dynamic mechanical analysis" instrumentation available for the development of specific test methodology in the determination of engineering parameters of selected materials, esp., plastics and elastomers, over a broad range of temperature with selected environment.

The methodology for routine procedures have been established with specific attention given to sample geometry, sample size, and mounting techniques. The basic software of the duPont 1090 thermal analyser has been used for data reduction which simplify the theoretical interpretation. Although clamp hardware was not available for the testing of 'liquid' resin systems, clamps were developed which allowed 'relative' damping during the cure cycle to be measured for the fiber-glass supported resin. The correlation of fracture energy 'toughness' (or impact strength) with the low temperature (glassy) relaxation responses for a 'rubber-modified'epoxy system was negative in result because the low-temperature dispersion mode (-80 C) of the modifier coincided with that of the epoxy matrix, making quantitative comparison unrealistic.

INTRODUCTION

The exciting technological advances generated by the space program are evidenced by the development of materials that operate at the extremes of the thermal environment - from the high temperatures experienced by the plastic materials which serve as ablative heat shields to the composite structures in the space telescope which must exhibit negligible expansion coefficients to cryogenic temperatures. Achievement of this vast range of the engineering successes is commensurate with the development of new materials having properties previously thought impossible - liquid oxygen-compatible high impact elastomeric resins-, of new processes and new analytical techniques which provide the engineer the necessary data for full utilization of the material properties in structure design. Books (1,2) have been written depicting these "space-age"materials and outlining recent developments in the synthesis, properties characterization and range of applicability of thermally stable engineering resins and of cryogenic compatible exotic plastics and elastomers.

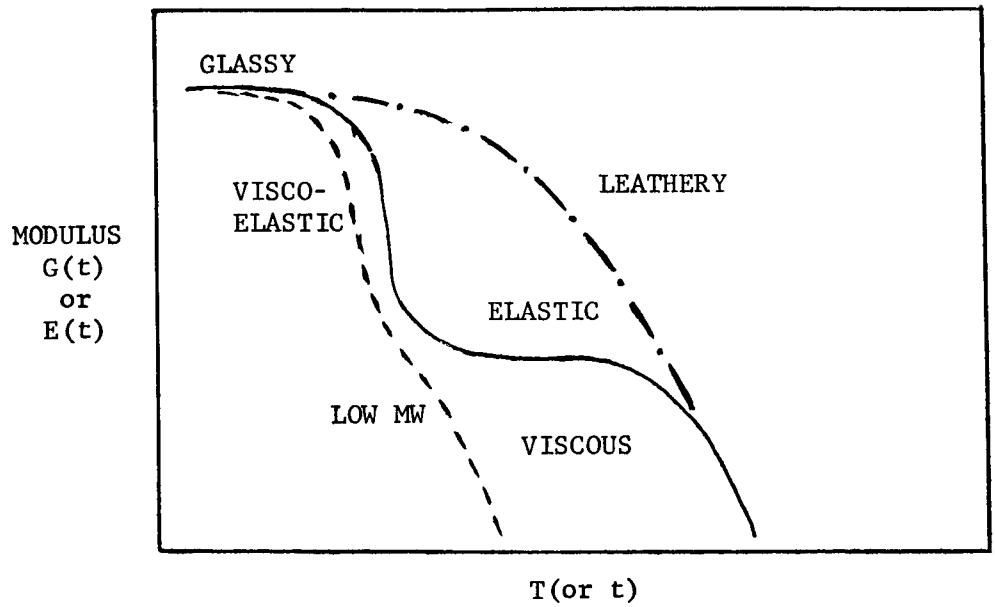
The high technology requirements for deep-space exploration, for extended periods in near-space, and for an over-riding need for energy conservation demand the development of new materials and controlled variability of the engineering properties of these new materials. Consequently, there remains a continuing need for fast, reliable accumulation of the materials engineering data to accelerate design and production of these space-age materials.

The method of dynamic mechanical analysis involves the study of the mechanical properties such as the dynamic storage modulus and the energy damping which define the stiffness and the mechanical energy dissipation (as heat) of the sample under sinusoidal or other periodic stresses. Since, for viscoelastic resins, the stress and the strain are not generally in phase (except at very low temperatures where the sample exhibirs brittle-like glassy behavior), these two parameters yield properties evaluation especially sensitive to the chemical and physical structures of the resin, to the influence of the 'thermal history' on the sample properties, and to the effect of processing conditions, e.g. molecular orientation and stress anistropy, on material stability (3).

This project was designed to utilize the dynamic mechanical analysis instrumentation available in the development of specific test methodology for the determination of engineering parameters of selected materials, especially for epoxy resins, over a broad range of temperature with selected environment.

DYNAMIC MECHANICAL ANALYSIS

The vast range of applicability of polymeric systems is a direct consequence of the wide variety and range of mechanical properties concomitant with these materials. These properties vary from those of viscous liquids to elastomeric solids, through the viscoelastic region, to hard and tough rigid solids. This behavior may be represented by graphing the modulus of the sample (tensile or shear) versus the temperature (or time) as shown.



A number of microstructural and compositional factors influence the magnitude of the moduli and the phase transition temperature, such as the molecular weight, the degree of branching, and the extent of crosslinking, the degree of crystallinity and the crystallite orientation (fibers), and for graft and block copolymers versus the polymer blends, to name a few. For example, the elastic response would not be observed in a low molecular weight sample which has no crosslinks and few chain entanglements (dashed line). The presence of crystallites would tend to mask out the glassy to elastic transition as shown by the (——•) curve above.

In addition to the behavioral factors given, the measured mechanical properties of a given system will be dependent on the type and on the speed of testing, the processing conditions and on the thermal history (stored internal stresses), and on the environmental conditions (humidity induced stress cracking in fatigue). The sensitivity of polymeric systems to temperature (or time) and to the rate of measurement is chiefly a result of the blend of viscous (segmental motion) behavior, in which the strain is proportional to the rate

of strain with viscosity being the constant of proportionality, and of elastic chain coil deformation behavior, in which the strain is proportional to the stress magnitude with Young's modulus (in tensile strain) representing the coefficient of proportionality. It is because of this viscous component of polymeric systems with some of the mechanical energy being converted to heat energy that comparison of mechanical properties and predictions based on such properties must always consider the magnitude of this energy dissipation by including correlation of the rate of strain with the specific stress-strain relaxation mechanism unique to the system.

The concept of 'dynamic mechanical analysis' (DMA) was originally developed more than forty years ago by Mooney and Gerke (4) in which a torsion pendulum was used to investigate the adiabatic heat buildup phenomenon in tires. Nielsen and Buchdahl(5) studied the effect of plasticizers on the glassy transition in polyvinyl chloride and the damping behavior in high-impact polystyrene some thirty years ago using a similar torsion pendulum. The use of the pendulum-based type of instrumentation has been expanded primarily by Gillham and Lewis (6) using glass-fiber braids as mechanical support for uncured liquid resins to allow indepth analysis of the complex mechanism of thermoset cure reaction. The early use of the torsion pendulum by McCrum (7) and by Sinnott (8) of DuPont has evolved into the development of the current modular system for thermal analysis by DuPont Instruments (9-11).

The DuPont 982 Dynamic Mechanical Analyser used in conjunction with the DuPont 1090 Programmer/Data Thermal Processor and with included software provide a system characterized by simplicity of operation with a wide range of materials from soft elastomers to metals and ceramics. A scope of temperature (-150 to 500 C) and time selections may be programmed with marked selectivity of instrument readout (temperature, time, fundamental resonant frequency, and mechanical damping) conversions through preprogrammed software calculations yielding quantitative values of storage and loss moduli, tan delta, and logarithmic functions of these parameters. The software routines allow automatic compensation for sample end effects,instrument compliance, and instrument damping.

The thermal processor system collects and stores real time data in a separate disk drive unit and then plots continuous printouts or tabulated data on command. The complex data analysis routine calculates the standard viscoelastic properties such as tensile storage and loss moduli, tan delta and allows calculation of comparable shear moduli as well. The graphical reports and the tables of calculated or real time data are obtained in a form suitable for publication. The prinouts may be further customised using a custom-plotting format. Examples of both types are presented as Figures 1-3. In Fig. 1 there is represented the preprogrammed printout of the real time data for a standard reference sample of an ABS terpolymer.

There is displayed in Fig. 2 the calculated tensile moduli and tan delta for the same sample. The capacity to make comparison plots by recalling real time of calculated data from the disk storage unit for different samples and plotting on fixed axes is shown in Fig. 3 including custom modification to fully identify the samples. Another feature is given in Fig. 4 which contains calculated data in tabular form and with identification of axis specifications. Many other features of this analyser system are described in reference 11.

EXPERIMENTAL

In this section there is described the materials used in this work together with a brief description of the equipment employed. Also, there is included a step-by-step outline of the operation of the DuPont Dynamic Mechanical Analyzer instrumentation.

Materials: The epoxy resin used throughout this work was Shell Epon 828, a low molecular adduct of bisphenol A with diglycidyl ether having an epoxide equivalent of 5.1 equivalents per kilogram. The hardener, Shell Z, a misture of m-phenylene diamine and methylene dianiline, was added in stoichiometric amount. Both reactants were preheated to 60-70 C, mixed vigorously by stirring, evacuated several minutes under forepump vacuum, and poured into preheated aluminum molds which had been sprayed with Teflon mold-release agent. Samples for cure studies were poured directly into aluminum pans. The resin was allowed to set at room temperature for around sixteen hours, and heated for variable times with a standard cure for mechanical analysis of two hours at 100 C and two hours at 150 C. Samples were removed from the molds after cooling, machined or ground to the desired form and polished with 600 sand paper.

A rubber modified sample was prepared by mixing into the above system 25 phr of WC-8006 (Wilmington Chemical Co.), an epoxy-terminated acrylonitrile-butadiene rubber, and given the same cure cycle.

Equipment: Test sheets of the resin were made by casting into and curing in aluminum molds measuring 20 cm by 10 cm by 0.32 cm (0.125 in) inside dimensions. The milled-out section of the mold was one cm thick and was faced with a 0.64 cm polished slab of aluminum plate. These were secured with four C-clamps, heated to 41 C in an air oven and the warm resin was slowly poured into the slightly tilted mold.

The instrumentation for the measurement of dynamic mechanical analysis was the DuPont 1090 Thermal Programmer/Data Processor, the DuPont 1091 (dual)Disk Drive unit, and the DuPont 982 Dynamic Mechical Analyzer (see reference 11) with appropriate software (AdvDMA V1.0 data reduction program).

Brief Manual of Operation: Power should always be supplied first to the 1091 Disk Drive unit to prevent disk drive hangup which may occur if the 1090 Processor unit is turned on first. Shutting down and turning back on in proper order will eliminate the hang up should it occur. After a rapid internal self-analysis of the instrument, the display board shows date and time which must be accepted by depressing the Yes key (not Enter). The display then leads the operator through the necessary steps required to provide the required information for real time data obtainment. The final step in this programmed sequence in the Y-axis shift. The New File key is depressed which will automatically add one file unit to the last one

used in either obtaining real time data or in data analysis. Should this new file number already contain data, an error notation will be displayed and the basis for this error will be presented by activation of the Help key. If the operator is uncertain of the correct file number, depressing the File Control key and following the indicated steps allows data files to be identified, deleted, method or sample identificationto be changed, and files to be protected from errant deletion. At any time the file contents may be displayed or printed with the identified keys in the List section of the board.

Once the file number has been correctly entered, chart paper must be in place with the chart load red light out before plotter will operate. Depressing the chart Label key will print out and label the axes as entered during the sequence above and will print sample identification, date and time (see Fig. 1). Then the Pen-up key is depressed, which activates the pen to start plotting at the start of the run. The steps in this paragraph may be bypassed if a plot of real time data is not desired. It will be stored and can be recalled as soon as the run is complete.

Actuating the Store key will involve the data storage system. (Should the display already show St or Store on the right side under indicated temperature, depressing the Store key will negate data storage - press again to reactivate). It is mandatory that all entered information be correct at this point because it cannot be changed once the test procedure has been activated by the SET-UP key.

Before the Set-up key is activated, the sample obviously must be in place, centered in the clamps and torqued to 10 in-lb for hard samples and 5 in-lb for soft elastomers. The metal shield must be placed around the sample and the thermocouples - CAUTION - placed very close (1-2 mm) from the sample near the driving arm. WARNING! The clamp screw holding the ceramic thermocouple leads should be carefully tightened with sufficient force ONLY to make if difficult to slide the ceramic rod. Then locking pins are removed from the arms after making sure the arms are parallel - use Length Adjust which slides the driven arm to make parallel - and replace the cover and slide into place the Dewar-type oven assembly and finger tighten connection screws.

With the Y-axis mode reading in millivolts, the display (push Display Axis key) will give the residual load on the LVDT and should be adjusted to zero ± 10 mv using the LVDT slide-arm wing-nut screw on the back of the module with the mode knob reading Align and 2 showing on the Osc Amplitude potentiometer (o.2 mm amplitude) and 35-40 for A/Z Gain. With a rigid sample in place, turning the mode knob to Cal will cause automatic zero-null of the LVDT. (This step is ommitted for non-rigid unsupported samples.) The mode knob is turned to Quant. You are now ready to start the test by depressing the Set-up key, which brings the sample to the preset temperature (displayed temperature may not be exactly the same as the control temperature)and when Ready appears in the lower right corner of the display, actuate the Start key and sit back and relax. The display will indicate when the test is complete. The mode knob on the 982

module should be returned to Align and cooling gas may be introduced to hasten cooling of the oven. Otherwise it takes about thirty minutes to cool to allow sample removal.

For normal type runs using similar type samples, a short hand method follows: with measured sample in clamps, module cover closed with oven in place, and storage disk in disk drive 1

1. Zero LVDT millivolt readout and turn mode to Quant.
2. Actuate Sample ID (Param) and enter data.
3. Actuate Method (Param) and enter data.
4. Enter Axis information (X&Y signal,range and shift).
5. New file selection.
6. Chart paper in place and red light out. Label and Pen-up if real time plot is desired.
7. Heater button IN (upper panel), actuate store, set-up and start.

The system is now in an automatic mode and will begin the test when the pre-set temperature is reached.

Low Temperature Operation: When the test involves below ambient conditions, the DuPont LN_2 tank assembly is attached to the back of the 982 module and the Tank Pressuriser is opened two full turns to give 5 - 7 psi readout - allow 15 min for equilibration. The Liquid valve is opened one-half turn until the temperature reaches -60 C and then closed to one-quarter turn open and the Cool Gas valve opened one-eighth turn. Actuate the Set-up key 30 degrees above start temperature - Ready will be displayed when the correct temperature is reached. Try to maintain the Ready condition at preset temperature for several minutes with the oven heater voltage reading 10-20 volts by slight adjustments of both valves. Press Start and hope that the oven heater voltage stays in the 10 - 20 volt range which will give linear time-temperature dependence. AVOID drastic valve changes. Don't be disappointed if the desired linearity is not always achieved. For an example of how bad it can get, see Figure 6. GOOD LUCK!

Data Playback and Analysis: Actuate Playback Set-up key and Enter the (correct) file number. Select the data to be plotted (X and Y - three Y axis selections)and check for chart load condition. Actuate the AutoScale key (generally) or Fixed Scale and plotting begins. Autoscale selects the axes so that all data points are included. The primary value of real data plotting is for a check of time-temperature linearity and of transition temperatures because the absolute magnitude of instrument readout depends somewhat on sample dimensions, longer and th;icker samples give lower frequency, etc. The calculated data, tensile storage and loss moduli and tan delta are independent of sample dimensions - see Figure 7 - so these values are used for sample comparisons.

The data analysis software is actuated by the Data Analysis Set-up key which leads the operator through the selection of type of data readout, continuous or tabular printout - see Figures 3 & 4 - and Auto- or Fixed scales. In this sequence the operator may select all or part of the test information for display so it is convenient to Autoscale the data and use this printout to set range values for fixed scale to allow ease of comparison with other data from other

files or allow expansion of any portion of the test results - see Figures 8 & 9.

The custom-format of the printout is engaged using the Control Param key - enter 5 and the desired information and set the X and Y axis offset. Examples of custom plottiing is shown in the Figures 4, 5, 6, 8, and 9.

The many other options included in this instrumentation are detailed in the respective manuals with which you should be familiar and which you should consult whenever questions arise.

RESULTS AND DISCUSSION

The DuPont Thermal Analyzer system has been demonstrated to be a reliable means of obtaining DMA examination of a series of polymeric materials from the thermoplastic ABS resin, Figures 1 & 2, the perfluorinated Kalrez elastomer, Figures 3 & 4, the hybrid graphite-epoxy composite, Figure 5, the glassy and rubber-modified epoxy resins, Figure 8, and the cure study of an epoxy resin, Figure 10.

The sensitivity of this instrument system is shown by the comparison of two runs on the Kalrez elastomer in which a small loss modulus peak was observed in the test piece which previously had been strained to break but the peak was absent in the test piece cut from the same sample which had no strain history. This result also illustrates one application of this type of analysis - that of the effect of processing conditions on the mechanical behavior.

The reprocibility of DMA test data has been thoroughly examined by testing duplicate samples in the study of the effect of addition of rubber-modifier to the base epoxy. The curves shown in Figure 8 represent superposible curves for each system. Also, one series of test runs on the effect of continued heating on the glassy transition temperature - not shown - gave superposible data on three different samples, one of which was markedly different in sample length. Three different test runs using calibration standards of DuPont Lexan test bars were identical both for real time and for the calculated moduli.

Although the reliability of the instrument complex has not been tested in a long time frame, nevertheless, it is significant that over sixty different tests have been performed, in duration from one hour to six hours in the cure study, and over the temperature range from -150 to +200 C, without any instrumental difficulty. The self-analysis software programmed into the processor prevents operator error from generating excess on the components.

In summary, even though the DuPont 1090, 1091, and 982 instrument complex is highly sophisticated, it is, as claimed in reference 11, characterized by simplicity of operation, rapid turnover, a vast range of applicability and accurate and convenient representation of DMA data - all with a minimum of operator attention and effort.

The effort to utilize the DMA system to correlate the fracture surface energy of a series of rubber-modified epoxy resins was not successful as shown in Figures 8 & 9. The low temperature (beta) energy dispersion mode occurs at -20 C in the unmodified epoxy, resulting from the relaxation motions of the glycidyl segments.

As this also happens to be the glassy transition for the rubber modifier, the addition of the rubber to the epoxy matrix does not markedly alter the volume fraction of the low temperature dispersion segments. In fact, as shown in Figures 8 & 9, the unmodified epoxy has the highest tan delta, which may be due to a slight difference in the extent of cure as the stoichiometric ratio of epoxide/amine was the same in both systems with the rubber serving only to dilute the system and so retard the crosslinking reaction.

Some effort has been made to convert the clamps of the 982 module to accommodate a resin-coated fiberglass mat in the horizontal mode. Several variations were used with wire end-clips, bent to form a 90 degree bend, being most convenient since excess resin tended to seize the screws used in the more formal type of clamp and the end-clips were disposible. A typical result of the cure study is shown in Figure 10. It is clear from these curves that the maximum in the damping (dashed) curve corresponds to the transition temperature of the cured resin reaching the cure temperature (150 C). However, it has not yet been possible to identify the time of gelation, which should appear as a smaller damping peak at shorter times. The small shoulder at 15 minutes in Fig. 10 may result from gelation but additional effort will have to be made to justify this conclusion.

CONCLUSIONS AND RECOMMENDATIONS

The investigation of dynamic mechanical properties of polymeric systems is now, with the DuPont thermal analysis modular system, both immediately available and quantitatively reliable. The ease and speed of operation of this system should now allow almost routine of the mechanical properties of polymer resins and of composite materials as they become of interest in the diverse programs of this laboratory. With the impending arrival of other modules which utilize the DuPont 1090 and 1091 units, differential scanning calorimetry (DSC), thermomechanical analyzer (TMA), and thermogravimetric analyzer (TGA), the capability of the laboratory to characterize fully new polymeric systems and to obtain meaningful engineering parameters for structure design will be maximized.

Because of the significance of reliable characterization data, it is recommended that every effort be made to acquaint staff members with the full potential of this valuable thermal analysis equipment.

Further efforts at cure study should be delayed until the DSC and TMA instruments can be used since these methods have proved successful in obtaining positive results in this type of study.

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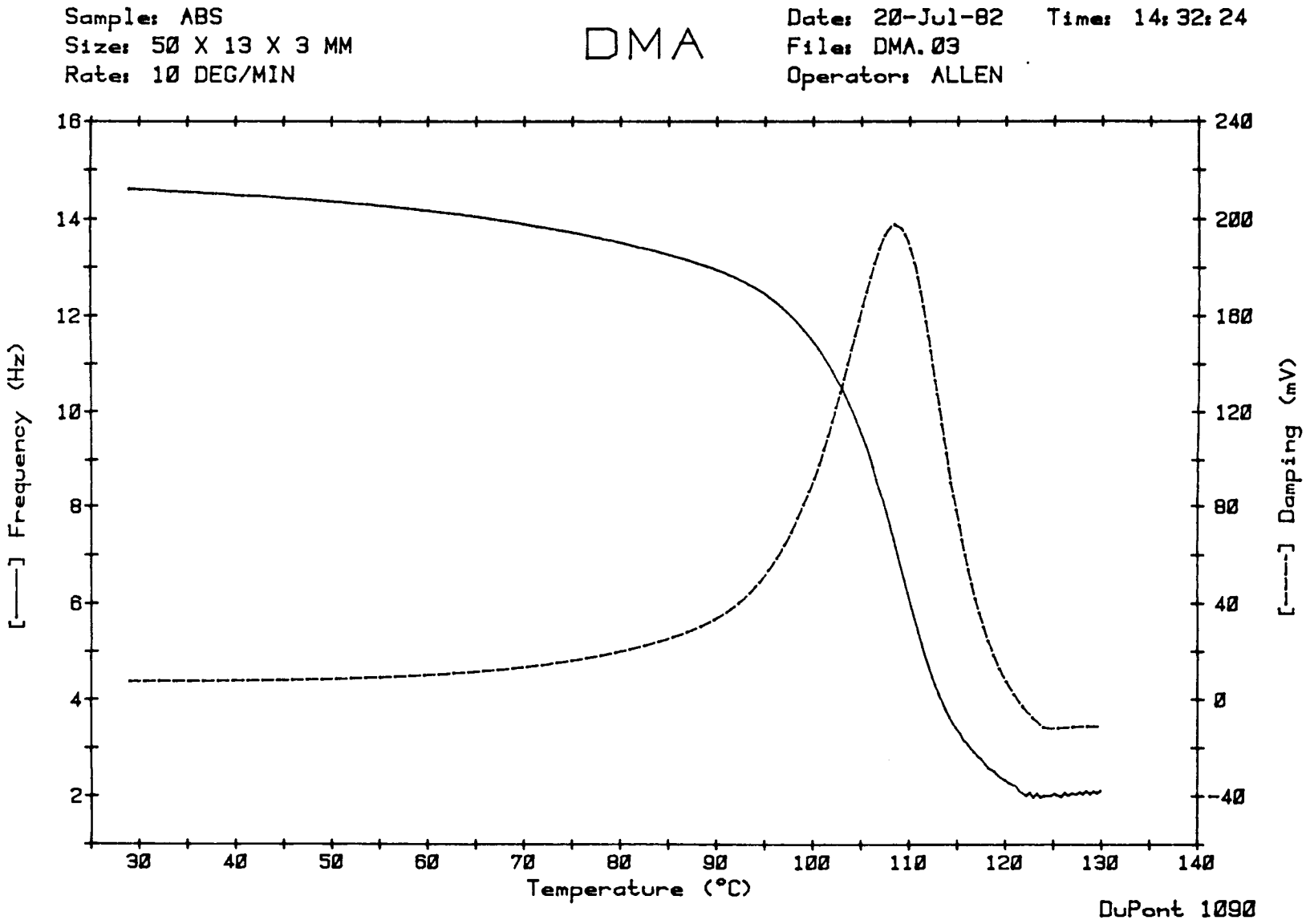

Figure 1. Real Time Data for ABS Resin

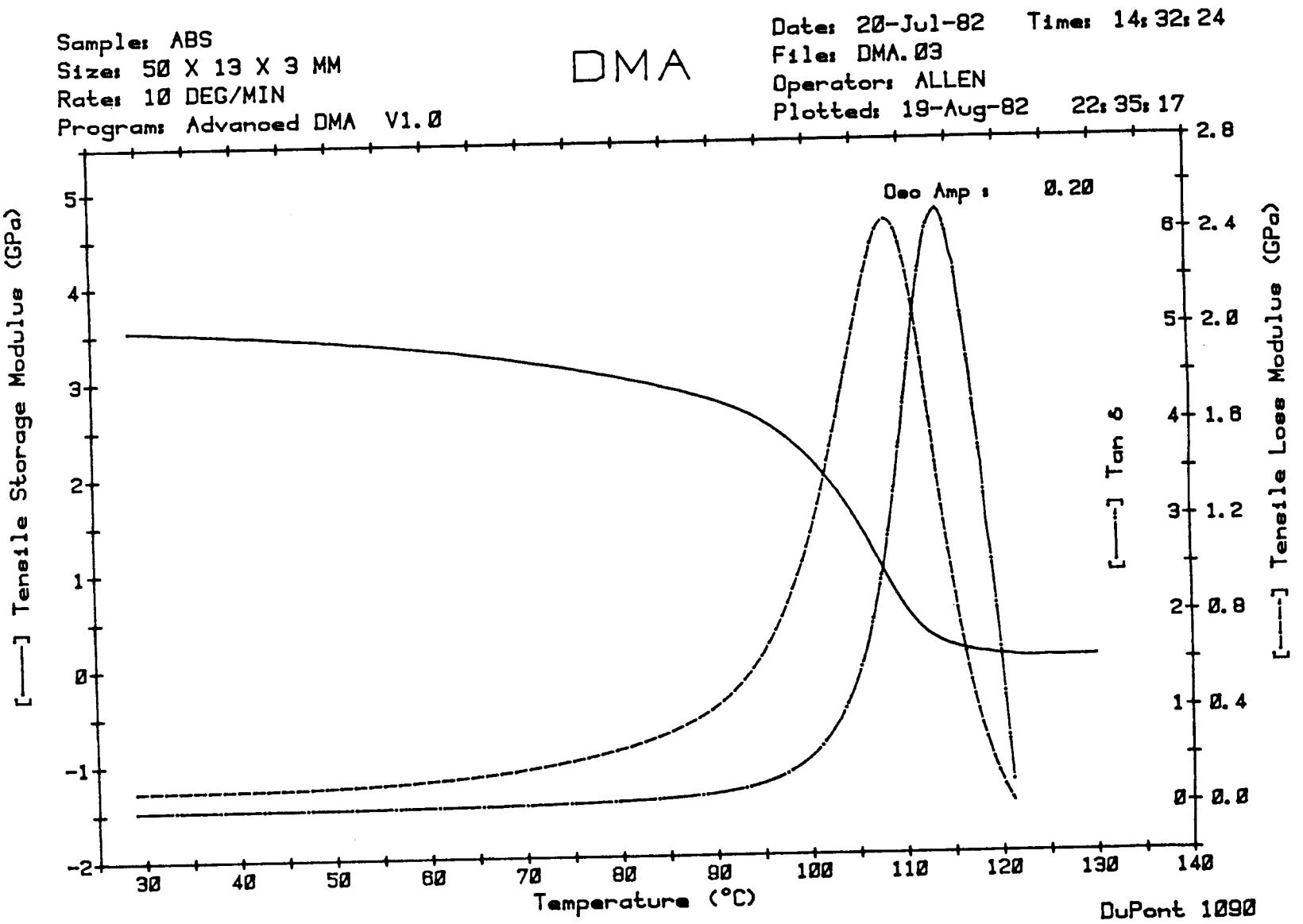

Figure 2. Calculated Data for ABS Resin

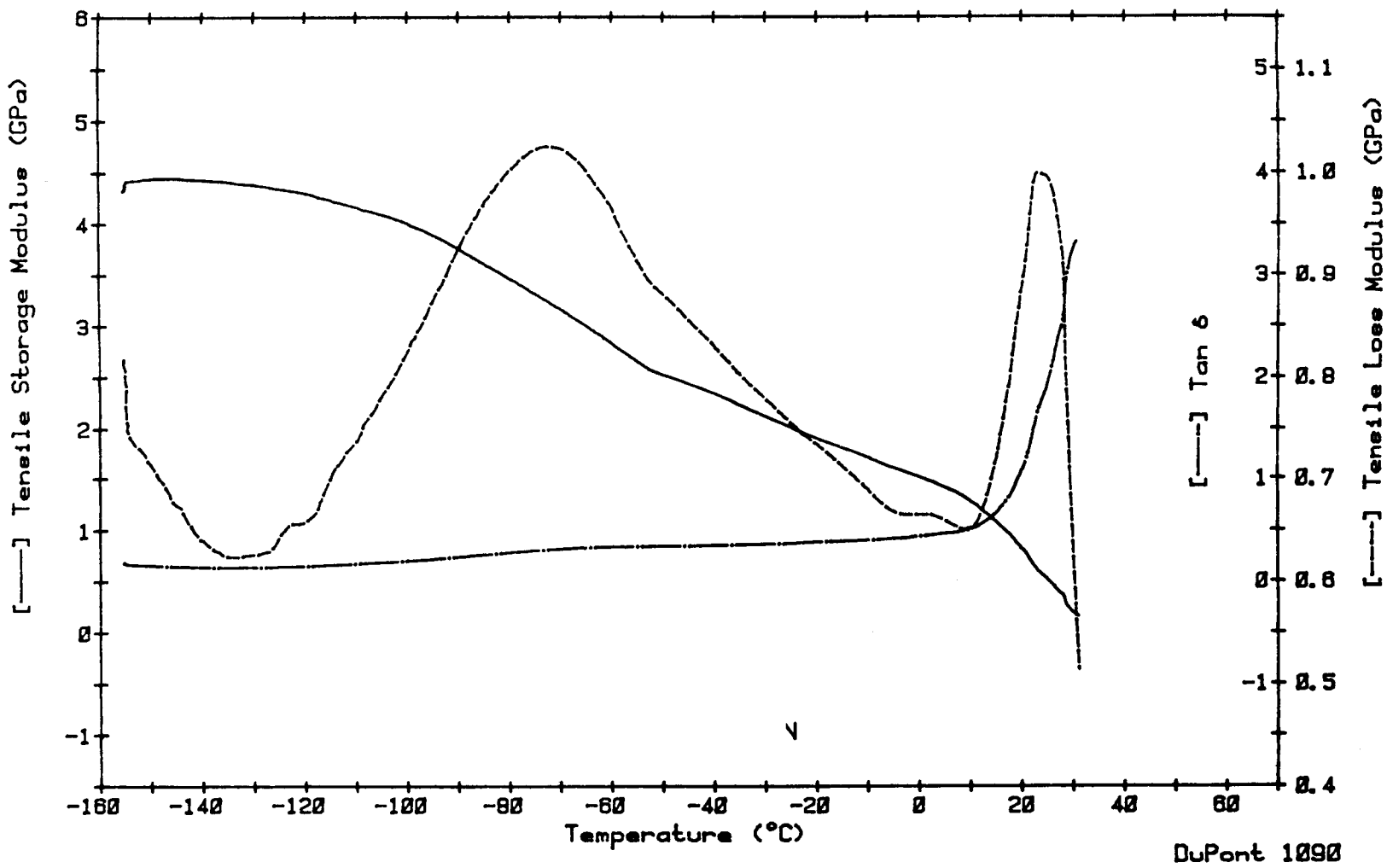

Figure 3. Dynamic Properties of Kalrez Resin

Sample: KALREZ BP-2
Size: 27.ØX9.2X3.3 MM
Rate: 5 DEG/MIN
Program: Advanced DMA V1.Ø

Date: 17-Aug-82 Time: 8:58:28
File: DMA.41
Operator: ALLEN
Plotted: 19-Aug-82 22:58:28

Temp [°C]	Tensile Store [GPa]	Tensile Loss [GPa]	Tan δ
-149.5	4.45	Ø.7Ø9	Ø.159
-139.8	4.43	Ø.641	Ø.145
-129.3	4.38	Ø.627	Ø.143
-119.8	4.3Ø	Ø.659	Ø.153
-109.7	4.17	Ø.738	Ø.177
-99.9	4.Ø1	Ø.825	Ø.2Ø8
-89.9	3.75	Ø.927	Ø.247
-79.9	3.48	1.ØØ	Ø.28Ø
-69.9	3.18	1.Ø2	Ø.324
-6Ø.Ø	2.83	Ø.967	Ø.342
-49.9	2.52	Ø.881	Ø.349
-39.8	2.33	Ø.829	Ø.358
-29.9	2.11	Ø.779	Ø.368
-2Ø.Ø	1.9Ø	Ø.735	Ø.386
-9.9	1.7Ø	Ø.689	Ø.4Ø5
Ø.1	1.51	Ø.666	Ø.442
1Ø.2	1.27	Ø.653	Ø.515
2Ø.2	Ø.811	Ø.892	1.1Ø
3Ø.Ø	Ø.194	Ø.633	3.26

	Range		Start/Shift
X-Axis:			
Time	2Ø.Ø	min/cm	Ø.Ø min
Temp	1Ø.Ø	°C/cm	Ø.Ø °C
Y-Axis:			
Time	5.Ø	min/cm	Ø.Ø min
Temp	1.Ø	°C/cm	Ø.Ø °C
Sig-A	2.Ø	Hz/cm	2 cm
Deriv-A	1.Ø	Hz/min/cm	Ø cm
Sig-B	2Ø.Ø	mV/cm	3 cm
Deriv-B	1.Ø	mV/min/cm	Ø cm

Figure 4. Printout of Tabulated Data For Kalrez Resin

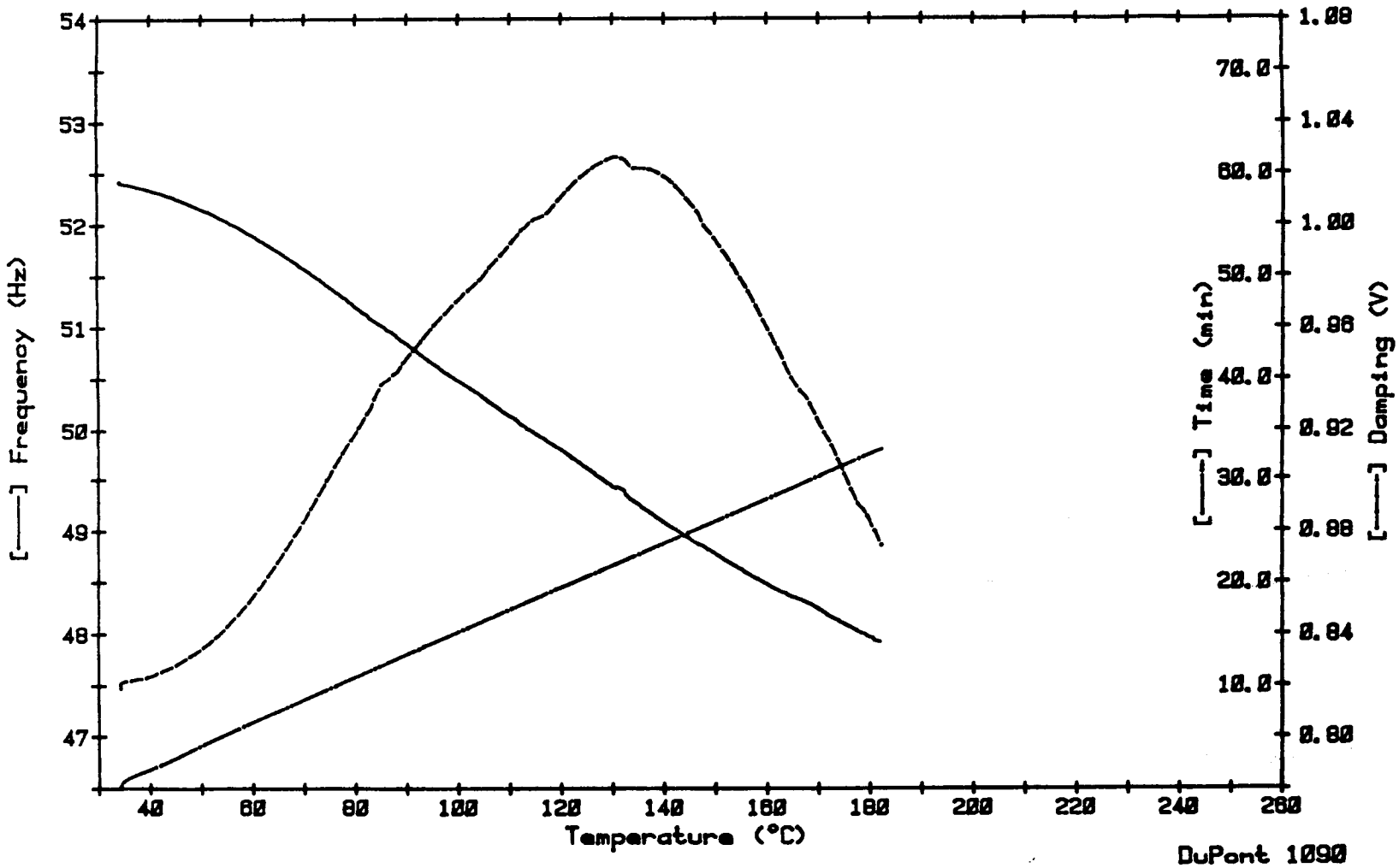

Figure 5. Real Time Data For Kevlar/Graphite/Epoxy Composite

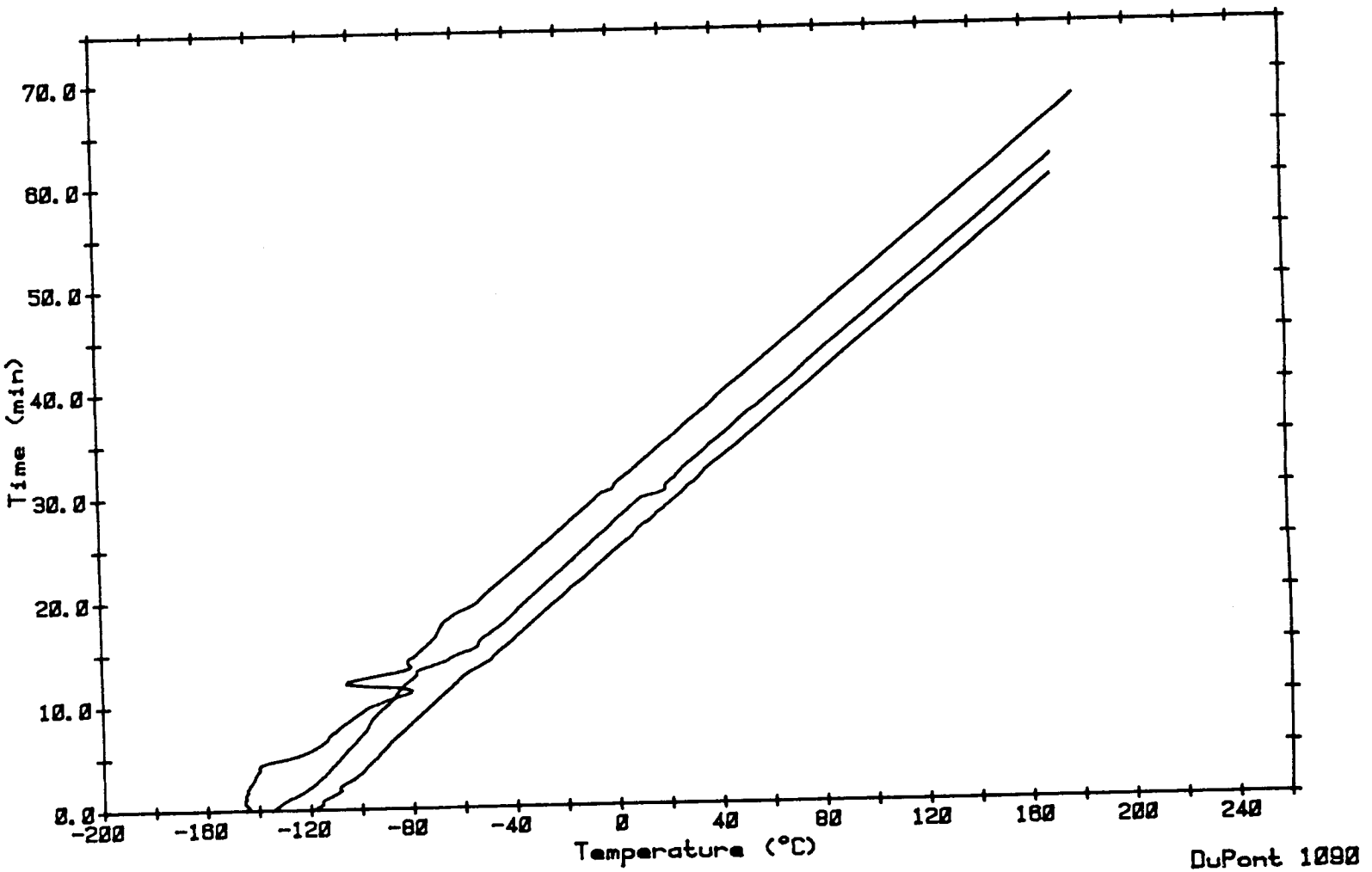

Figure 6. Examples of Good and Bad Control of Temperature In the Below Ambient Temperature Region

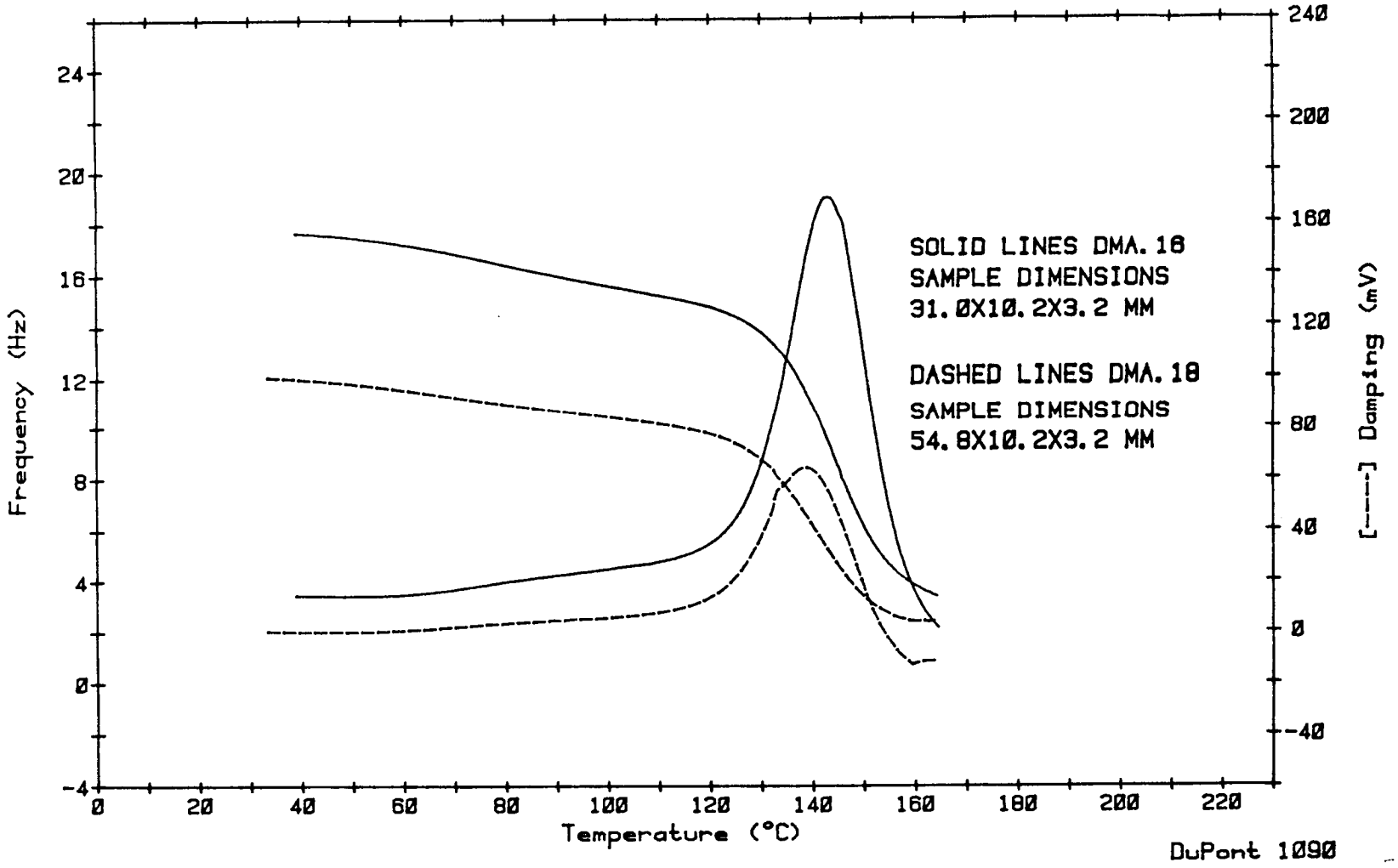

Figure 7. Effect Of Sample Dimensions On Real Time Data

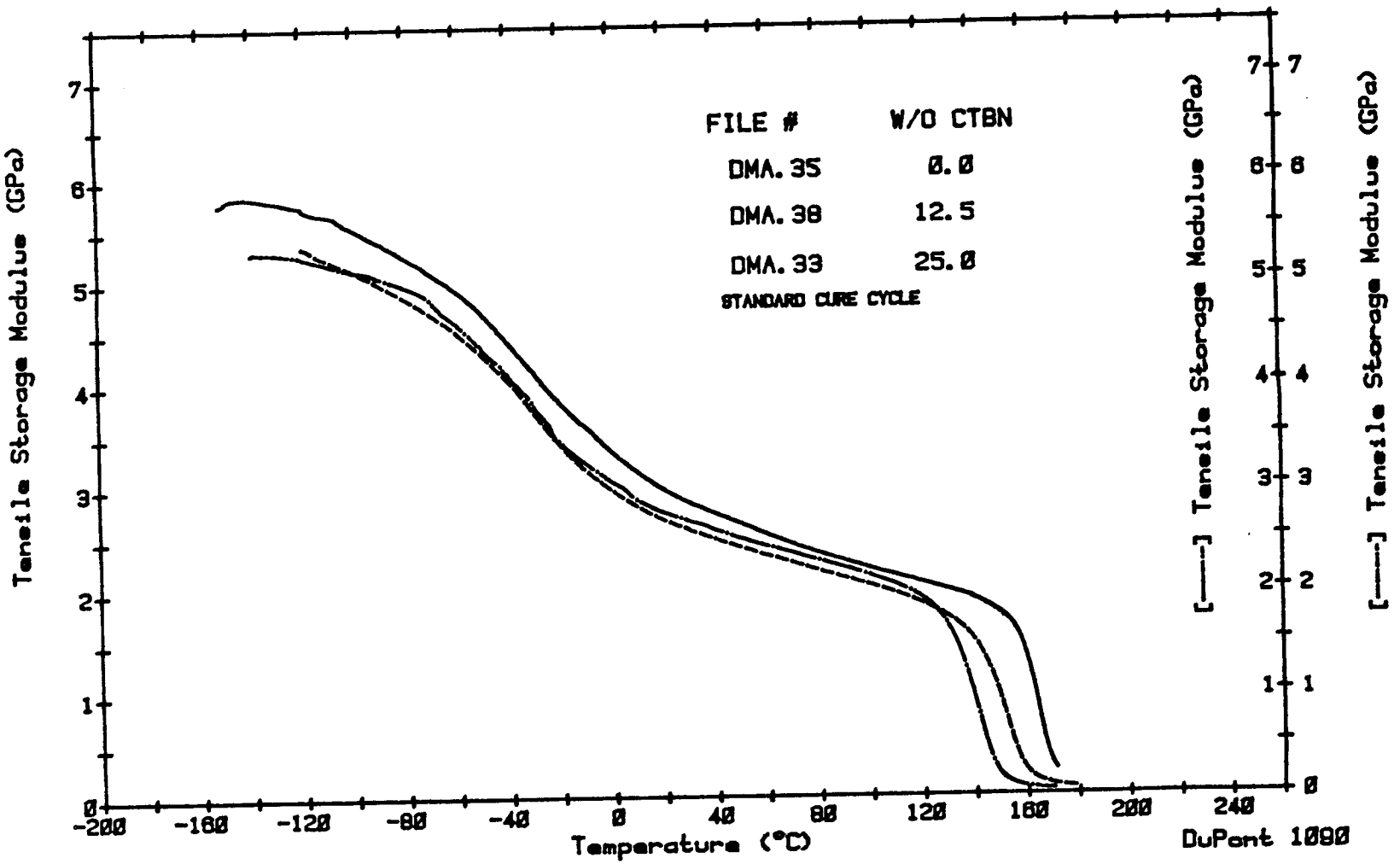

Figure 8. Effect Of CTBN Rubber On Tensile Storage Modulus Of EPON 828/Shell Z Epoxy

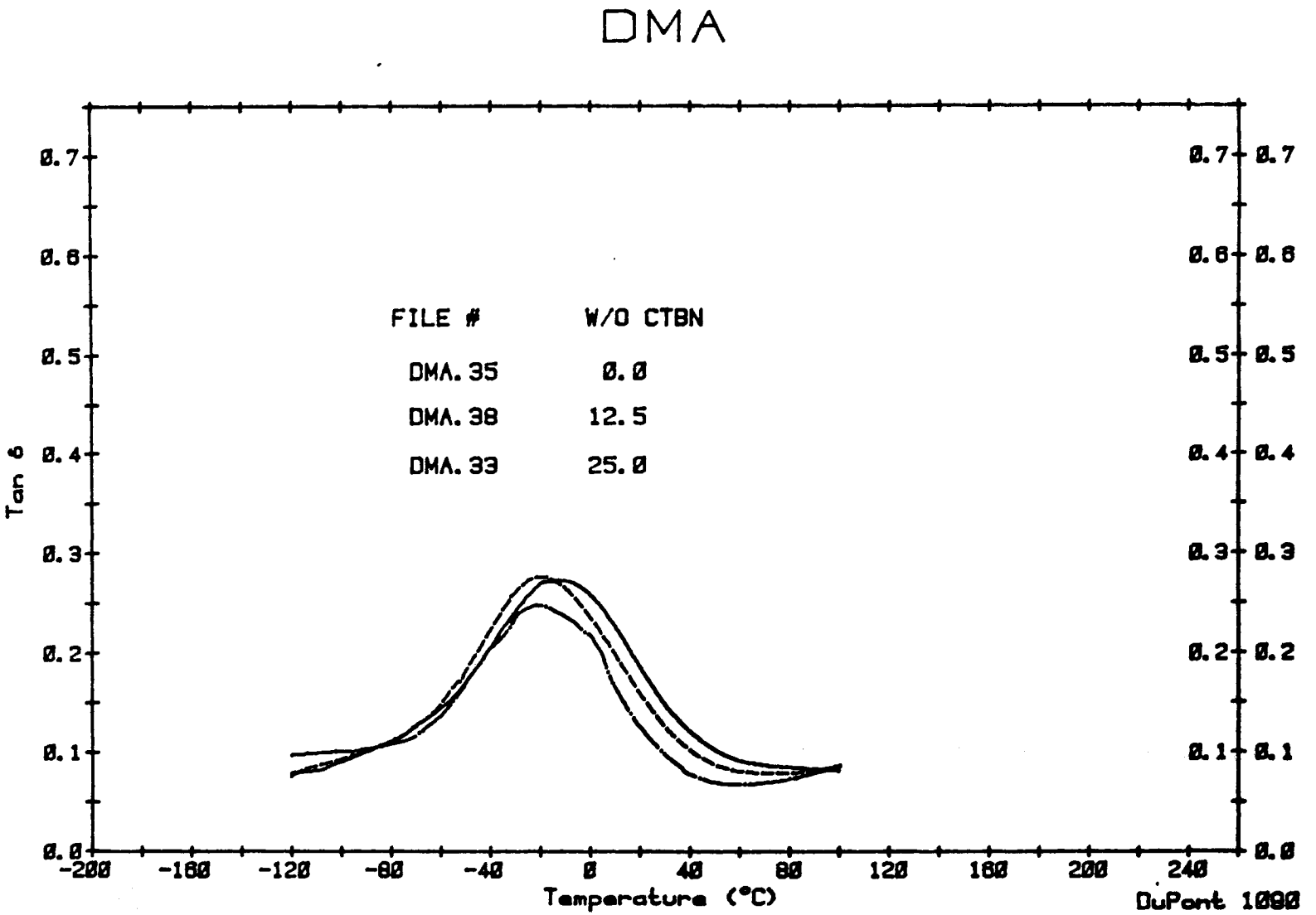

Figure 9. Effect Of CTBN Rubber On Tan Delta Of Epon 828/Shell Z Epoxy

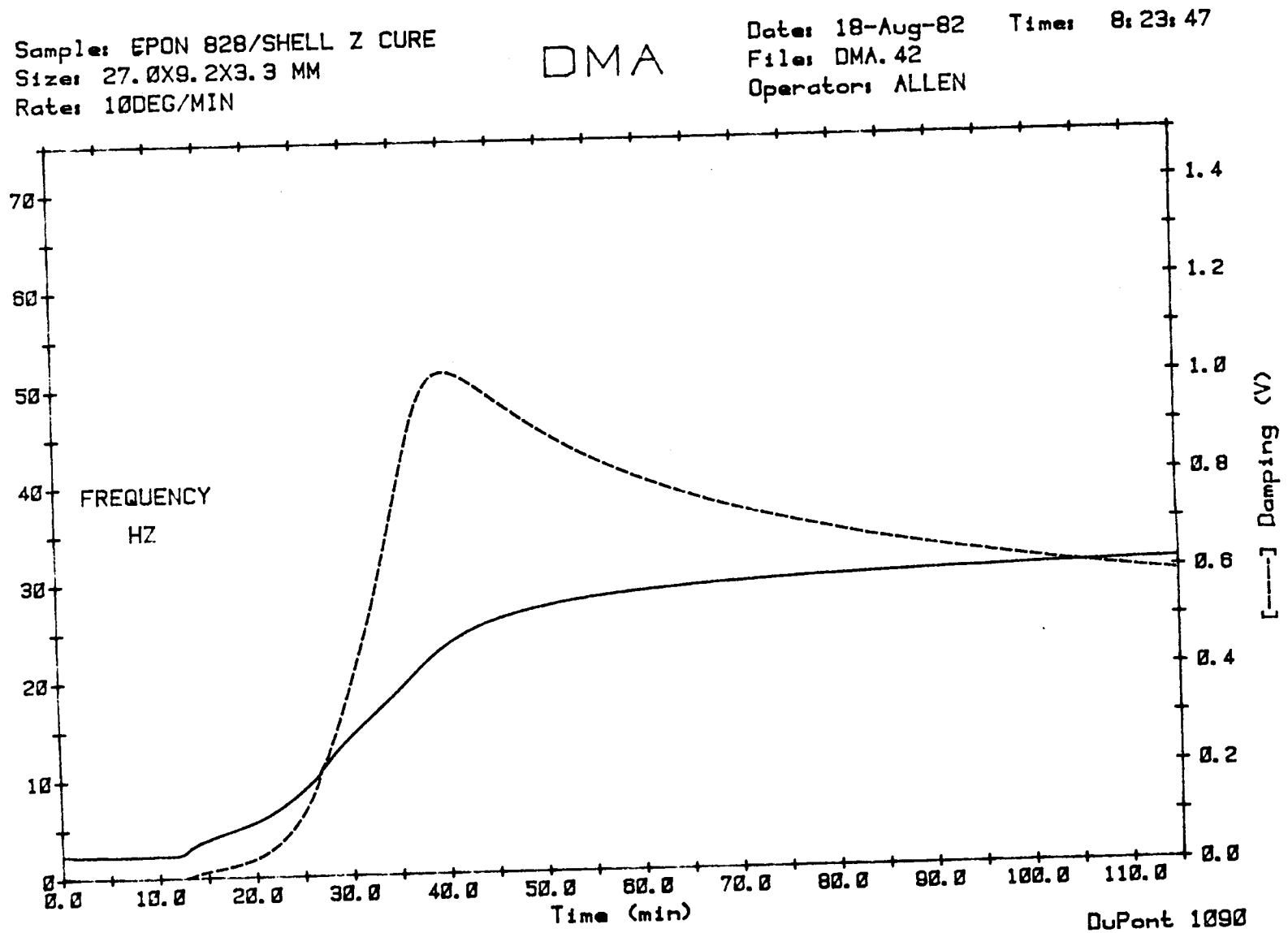

Figure 10. Rate Of Cure Study Of Epon 828/Shell Z
Real Time Data For Resin On Glass Braid