

Cross-Checking Between Dielectric Measurements, DTA, and Other Methods of Thermal Analysis in Research and Production

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Synopsis

Differential thermal analysis, or DTA, is a technique for determining the properties of materials from the thermodynamic and kinetic points of view. Dielectric measurement is also a powerful tool for probing the structure of materials, but from another direction. Dielectric analysis is a measure of the dipole response within dielectric materials to an applied electric field. This response is controlled by the spatial arrangement and viscoelastic properties of dielectric materials. Dielectric thermal analysis is being increasingly used in research and process control, offering the advantages of being non-obtrusive and easily instrumented and having a broad theoretical basis which can be correlated with results from other methods such as dynamic mechanical relaxation measurements, NMR, neutron relaxation, birefringence, and, of course, DTA. Because of the nonobtrusive nature of dielectric measurement, it can be run concurrently with other analytical techniques without disturbing their results. When dielectric analysis is run concurrently with other methods of analysis such as DTA, we often receive fresh insights and cross-checking on such behavior as polymeric crosslinking, molecular weight increases, and T_g -viscoelastic behavior in general. The results and conclusions drawn for such investigations are described.

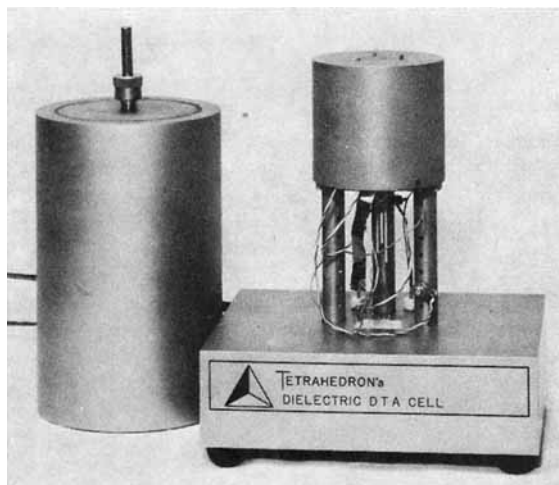
INTRODUCTION

Thermal analysis is a measurement of the properties of materials under conditions of changing temperature or time in various atmospheres. Differential thermal analysis, or DTA, involves comparison between the temperatures of the sample material and a thermally inert reference material, each of which is positioned in a metal block in equilibrium with its thermocouple. As the temperature of the block is programmed up or down, a signal proportional to the sample temperature is plotted out on the X-axis of an X-Y recorder. When the sample undergoes an endothermic transition such as melting, the sample thermocouple gives up heat through a diffusion process because the sample is cooler than the reference thermocouple. This produces a signal proportional to the temperature difference, which is plotted on the recorder's Y-axis. The area under these thermogram curves indicates the energy absorbed or given off.

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(a)



(b)

Fig. 1. Dielectric analysis equipment: (a) Audrey dielectric analyzer; (b) simultaneous dielectric-DTA cell.

In the past twenty years, DTA has gradually progressed from a qualitative analytic method to an instrumented technique whose uses span basic research, applied research, and the process control of materials. DTA gives insight into the structure of materials, particularly from the thermodynamic view.

Dielectric measurement is also a powerful tool for delineating the structure of materials, but from another direction. Dielectric analysis is a measure of the dipole response to an applied electric field. This response is shaped by such factors as spatial arrangement, molecular weight, and degree of crosslinking of dielectric materials such as polymers. Dielectric thermal analysis is being increasingly used in research and process control. It is a practical, nonobtrusive, and easily instrumented technique which has a broad theoretical basis and whose results can be correlated with those obtained from other methods such as dynamic mechanical relaxation measurements, NMR, neutron relaxation, and, of course, DTA.

Tetrahedron Associates has combined the methods of dielectric and differential thermal analysis in a single instrument called the Simultaneous Dielectric-DTA Cell (Fig. 1). With it, we receive fresh insights and cross-checking on such behavior as polymeric crosslinking, molecular weight increases, and T_g -viscoelastic behavior, in general. This simultaneous cell combines classical, high-performance DTA and dielectric probes. Used in conjunction with an automatic dielectrometer, the cell makes it possible to measure dielectric relaxation and thermodynamic changes, simultaneously or separately using a wide variety of samples. Drawing from our experience and that of several of our customers, we will describe some results and some uses of this form of cross-checking, in the hope that it will stimulate further activity in this field.

THE DIPOLE PROBE

Buried within dielectric materials is a particular atomic configuration, the dipole, which unobtrusively can be used to probe the molecular structure of the material. Dipoles will react in opposition to an imposed electric field, as shown in Figure 2, and this readily measured reaction can reveal much about the molecular structure of the material under investigation. Furthermore, an electric field can be unobtrusively coupled to a sample, whether in a test tube, reaction vat, or press. The changes that occur within a sample during a process can be monitored. Thus, using the dipole as our probe, we have a tool whose uses range from basic research to production, where results can be rapidly transferred from laboratory to factory.

Usually, a powerful analytic technique such as infrared spectroscopy will not fit into a production facility such as a laminating operation. Most IR analysts would be horrified by the prospect of resins and oils dripping over

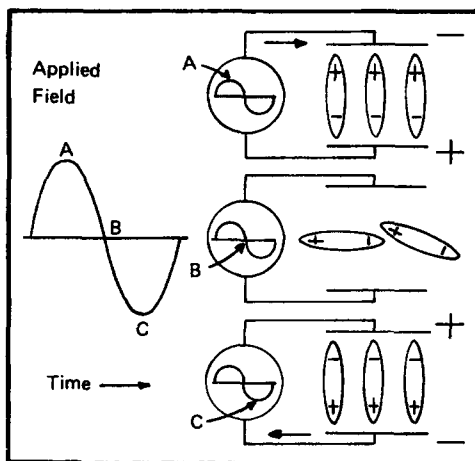


Fig. 2. Schematic diagram illustrating tendency of dipoles within a dielectric to align with an applied field.

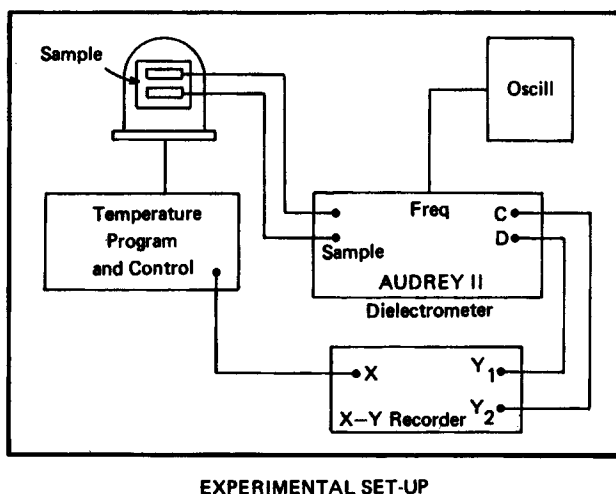


Fig. 3. Experimental setup for simultaneous DTA and dielectric analysis.

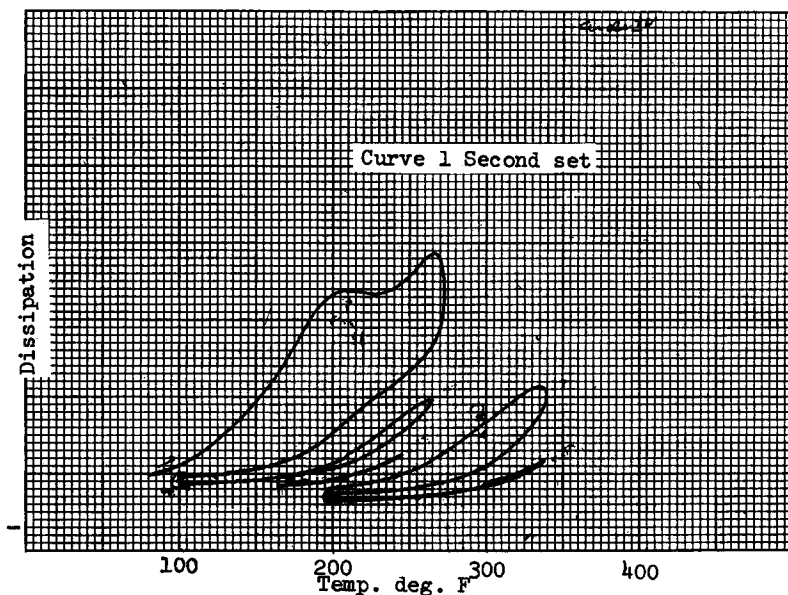
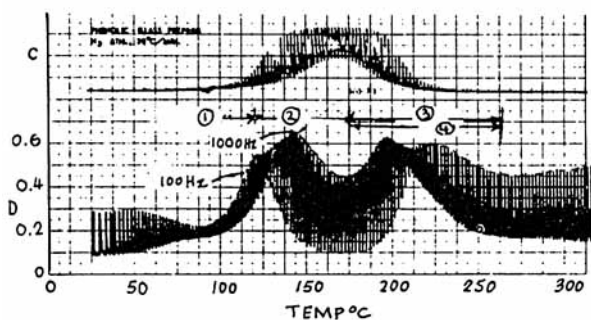
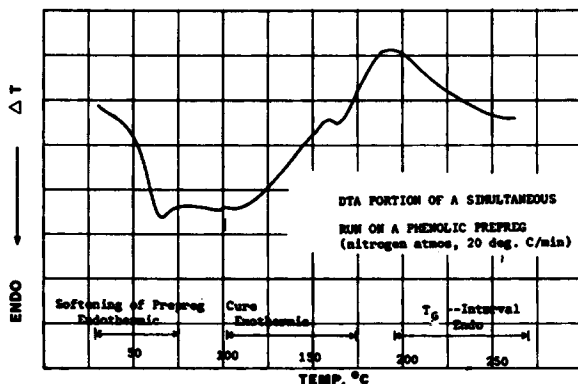


Fig. 4. Phenolic curing loop.

their optics. An electric field, however, can be cleanly wired into almost any fixture. For example, when the Audrey automatic dielectric analyzer is turned on, its alternating electric fields stimulate the dipoles to attempt to align, providing us with the necessary dielectric information. The extent of alignment is related to the material's dielectric constant and the power expended in tracking the field to its loss tangent, also known as dissipation factor.



(a)



(b)

Fig. 5. Simultaneous dielectric (a) and DTA (b) spectrograms of a phenolic-glass laminate. In (a) gelation is occurring in zone 1, curing in zone 2, postcuring in zone 3, and dielectric relaxations from other changes in zone 4.

An electric field of relatively low strength is unobtrusive and so permits dielectric measurement to be performed on a sample while some other measurement is being performed. Thus, we can crosscheck the results of dielectric measurements against information derived from other forms of analysis such as DTA, NMR and IR spectroscopy, and modulus measurements. Best yet, when we turn off our equipment, the interrogating field disappears, requiring no cleanup.

RESULTS OF SIMULTANEOUS ANALYSES

A typical experimental setup for simultaneous dynamic scanning dielectrometry (DSD)-DTA is shown in Figure 3. Simultaneous dielectric-DTA analysis requires a simultaneous test cell and an instrument for measuring dielectric properties. While any capacitance bridge is suitable for dielectric measurements, Tetrahedron's Audrey automatic dielectrometry instruments automatically record capacitance and loss tangent

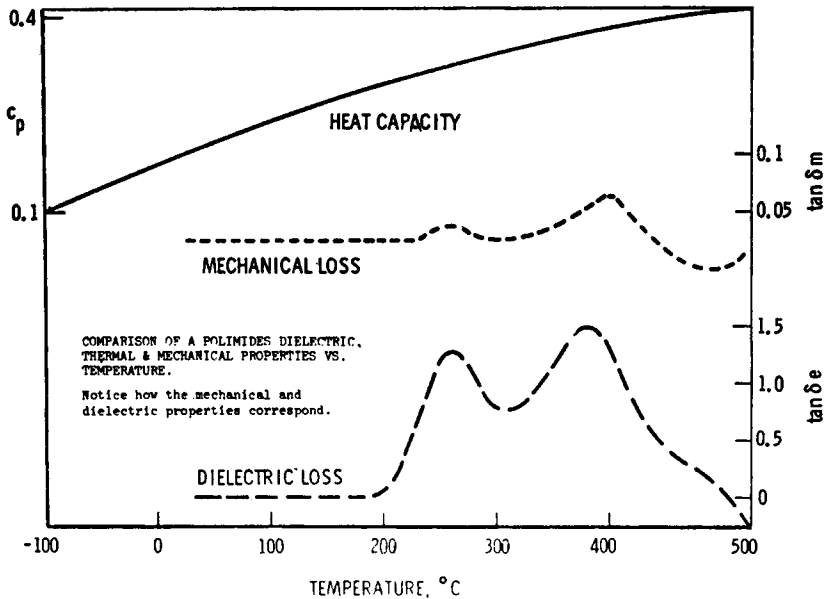


Fig. 6. Comparison of various experimental methods of analysis for polyimide film (du Pont's Kapton) (from Ref. 2).

over a range of frequencies and also provide a signal proportional to sample temperature.

If desired, Audrey may periodically be swept or stepped over its frequency range, providing us with a recordable output of the changes of capacitance C and dissipation D with time, temperature, or frequency.

Although phenolic resins were among the first polymers placed in production, numerous uncertainties in controlling their cure still exist, resulting in waste of material due to high scrap rates and failure to realize optimum properties. Figure 4 shows several dielectric thermal analysis cycles where a phenolic is heated to a particular temperature and allowed to cool. Each cycle produces a loop, and the circumscribed area of each loop decreases with each succeeding cycle, until finally the enclosed area drops to zero. At this point, the resin is fully staged or cured up to a particular temperature. By cycling to a higher temperature, further curing reactions are produced and we again generate a circle loop circumscribing a certain area. If we again cycle temperature up to a new limit, the heat-up and cool-down curves are seen to fall atop each other, with no circumscribed area apparent. We may then presume that the resin is again fully staged under these conditions. Circle curves, such as the one shown in Figure 4, give us a measure of the extent of cure or staging of a polymeric material.

There are several other ways of examining phenolics with simultaneous dielectric-DTA analyses. For example, continuously sweeping frequency at periodic time intervals over a temperature range at linear heating rates produces a "dynamic scanning dielectric" (DSD) spectrogram together with

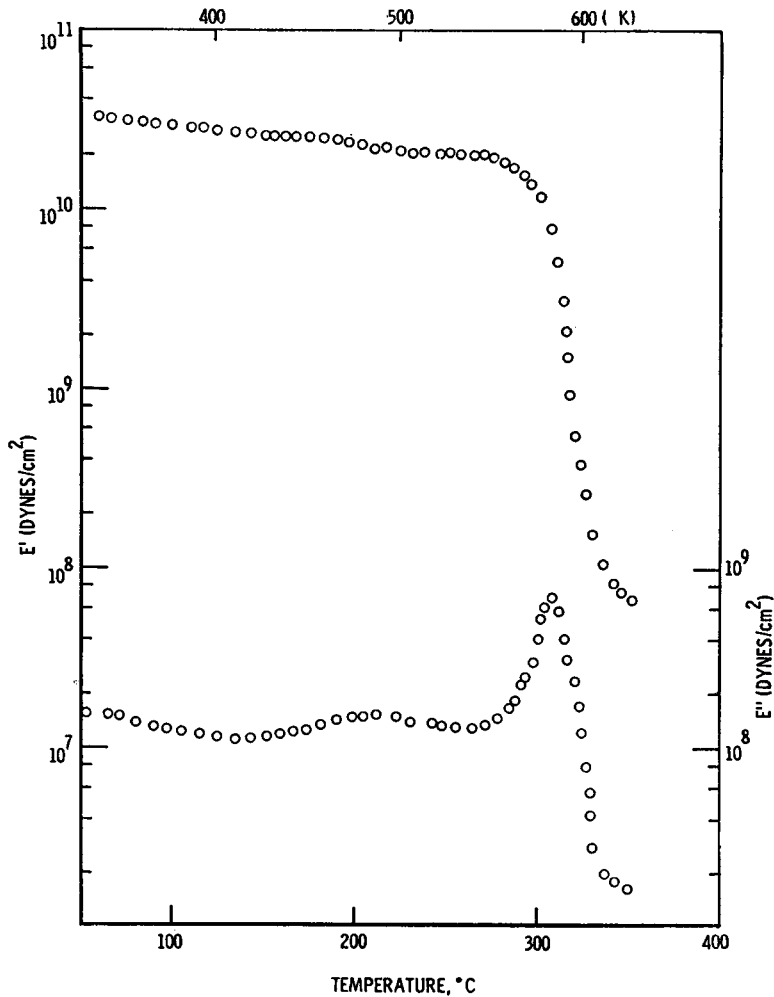


Fig. 7. Plot of storage modulus (E') and loss modulus (E'') as a function of temperature for polymer I (ref. 1).

a simultaneous DTA measurement on the identical sample.¹ By extrapolating log frequency versus $1/\text{temperature}$ it is possible to determine the activation energies for the dielectric relaxation process. Notice that in Figures 5a and b, which describe the changes of a curing phenolic resin, the DTA and dielectric records correlate well. This is not always the case. Occasionally, we obtain a dielectric and no DTA response, or vice versa.

In a paper on Dupont's Kapton film,² Wrasidlo has described the dynamic mechanical, dielectric, and DTA properties of the film, the latter two measured simultaneously. From these measurements and other relaxation data from various literature sources, a number of regions have been identi-

fied, including glass transition, possible polar endgroups, absorbed water, large-scale chain motions, and others.

Wrasidlo compared dielectric loss tangent, mechanical loss tangent, and heat capacity,² as shown in Figure 6. Notice that the dielectric and mechanical properties follow each other rather closely. The similarity between dielectric and mechanical property response to variables such as temperature and frequency is far from coincidental.³ This is quite often the case, dielectric and mechanical behavior both depending on polymer

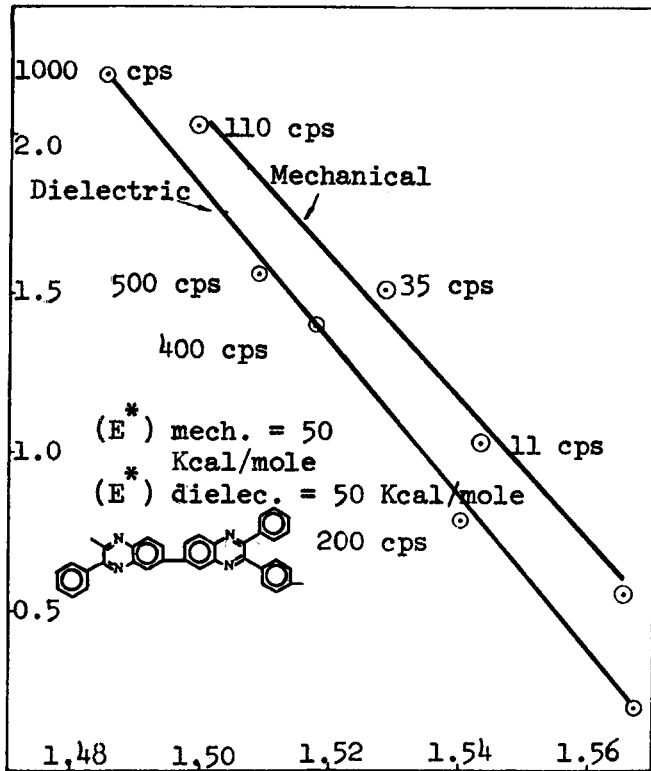


Fig. 8. Arrhenius plot for dielectric and mechanical loss maximum of a polyquinoxaline (ref. 1).

molecular weight, degree of crystallinity, viscosity, and temperature—viscoelastic properties in general. Indeed, the theories of dielectric and anelastic mechanical property behavior are similar, with electric field strength E being analogous to mechanical stress σ , dissipation D being analogous to mechanical strain γ , and dielectric constant ϵ being proportional to compliance J (J is the inverse of the familiar shear modulus).

The lack of any peaks or discontinuities in the heat capacity curve indicates the absence of any molecular motion which would lead to transitions such as glass or melt transitions. X-ray Laue patterns of a film

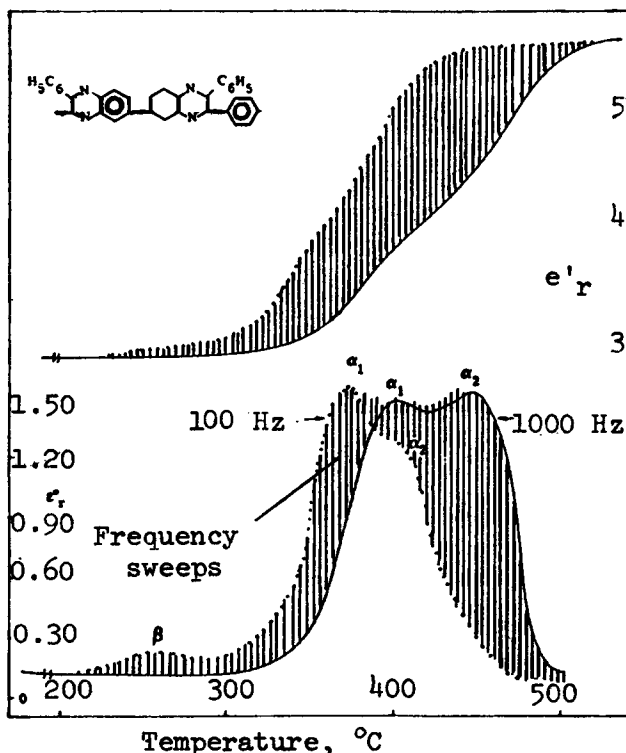


Fig. 9. Plot of relative dielectric constant (ϵ'_r) and loss factor (ϵ''_r) as a function of temperature with frequency as a parameter (ref. 1).

sample indicated the lack of crystallinity, confirming the absence of any heat of melting in this polymer (i.e., thermodynamic crystallinity).

Wrasidlo¹ also examined dielectric and mechanical relaxation and DTA response for a series of aromatic polymers. His findings are summarized in Figures 7 through 10. The temperature-versus-modulus plot (Fig. 7) shows a maximum dispersion of E' at 398°C. A major phased transition is suggested by the drop in dynamic storage modulus from 10^{10} to 10^8 dynes/cm², which is a physical transition from a glassy to a leathery state. The activation energy for this process was determined from an Arrhenius plot shown in Figure 8. The activation energies determined for the modulus and dielectric measurements (see Figs. 7 and 9, respectively) were 50 and 56 kcal/mole, respectively. From this it was concluded that the high-temperature dielectric and mechanical dispersions were basically the same relaxation mechanism and were probably due to the onset of micro-brownian motion of the main chains from a frozen state, involving the cooperative diffusional motion of large-chain segments.

The dielectric and mechanical relaxation loss spectra are summarized in Figure 10. The shoulder at 420°C in the 110-cycle dielectric relaxation

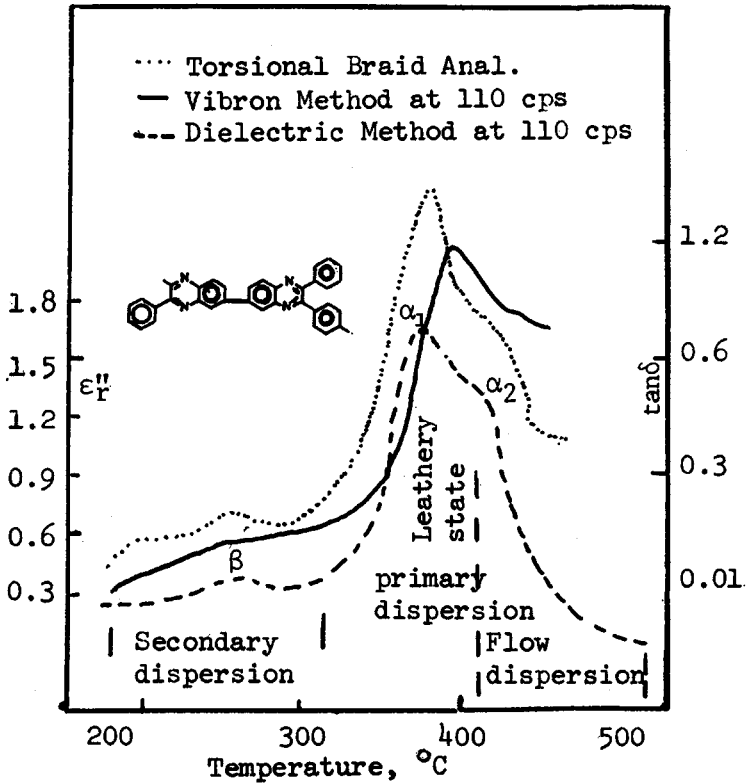


Fig. 10. Comparison of mechanical with dielectric loss spectrum (heating rate 2.5°/min) (ref. 1).

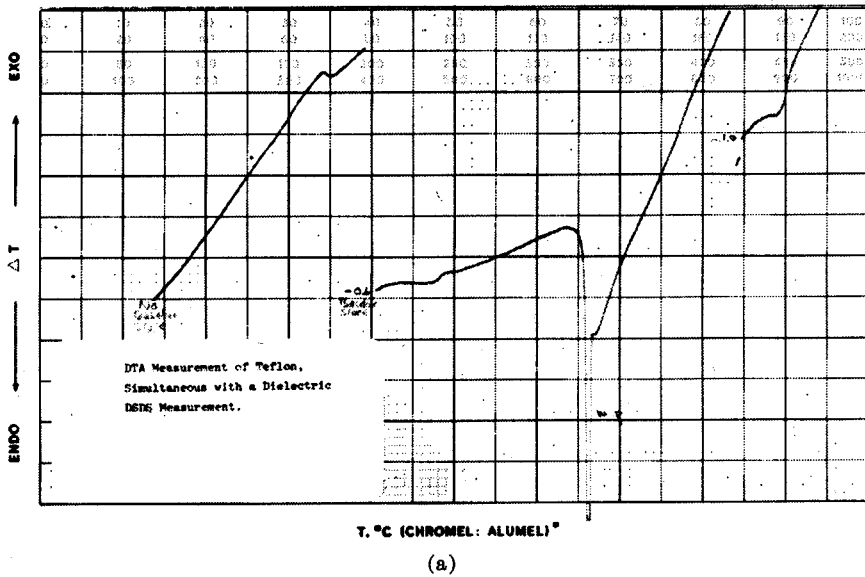
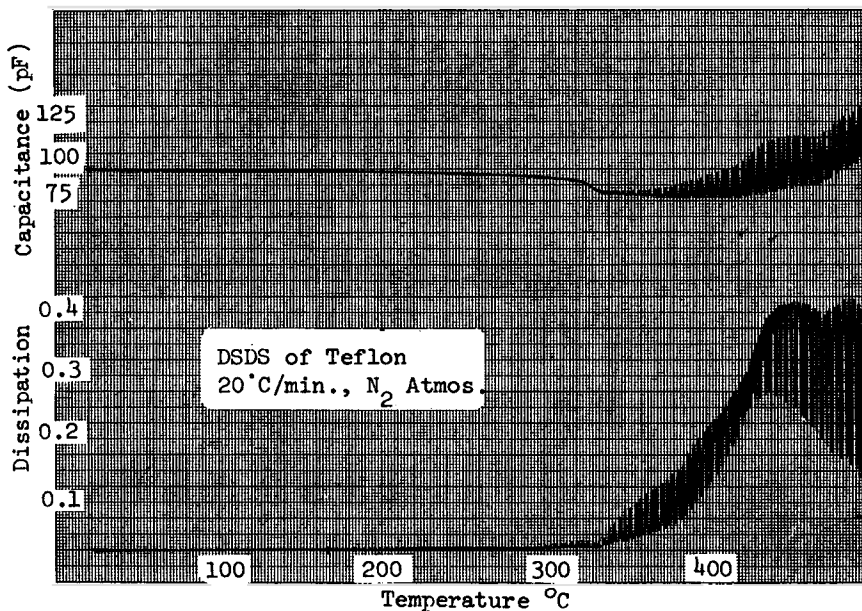
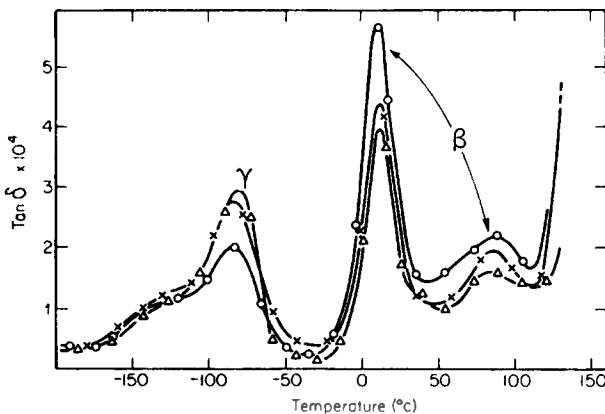


Fig. 11. (continued)



(b)



(c)

Fig. 11. DTA and dielectric properties of Teflon: (a) DTA measurement of Teflon made concurrently with a dielectric DSD measurement; (b) DSD analysis of Teflon (heating rate $20^{\circ}\text{C}/\text{min}$, N_2 atmosphere); (c) variation of the dielectric loss tangent with temperature (below 120°C) at 1kHz for three samples of PTFE. The β and γ relaxation regions are indicated: (x) sample I, nonheat-treated commercial sample; (Δ) sample II, most amorphous; (O) sample III, most crystalline. (From ref. 4.)

spectrum and at 430°C in the torsional braid spectrum is called the α_2 peak. It occurs in the fusion range of the polymer and is associated with a relaxation mechanism in which the polymer chains are in unison untying their entanglements.

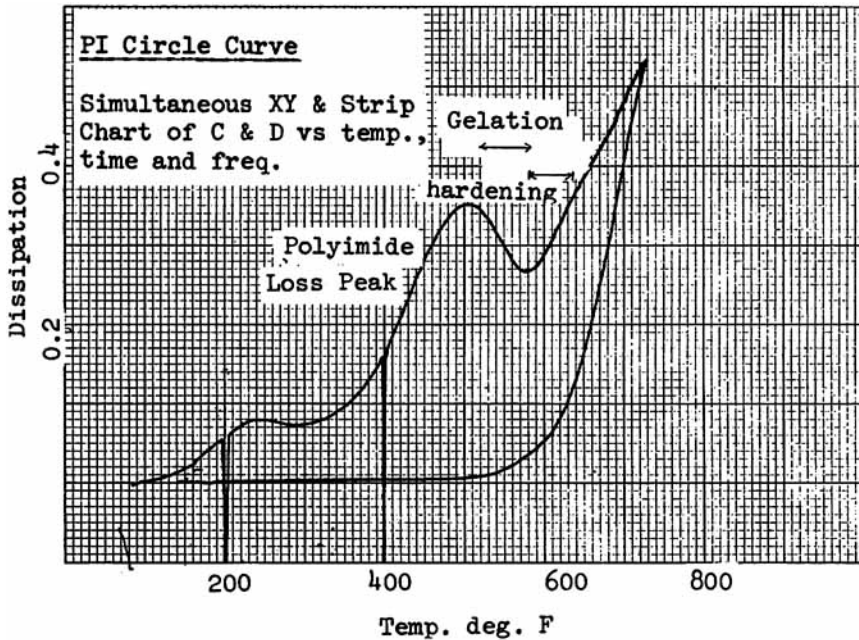
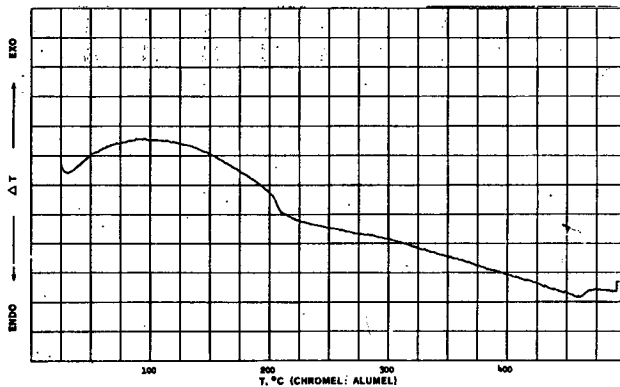


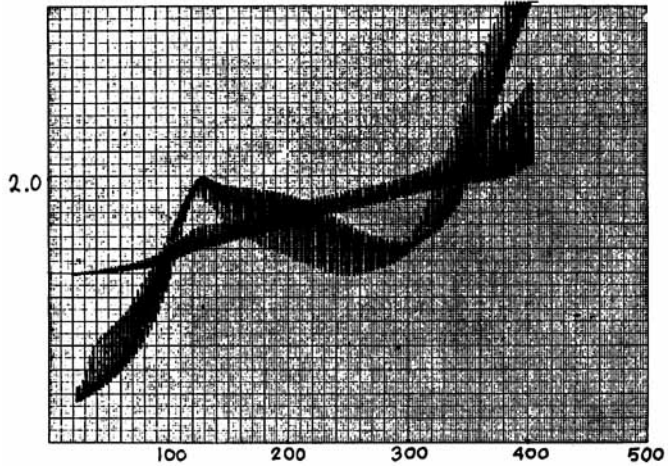
Fig. 12. Polyimide resin dissipation vs. temperature circle curve.

The DTA and dielectric behaviors of PTFE polymers such as Teflon are most interesting. In Figure 11, some aspects of the DTA and DSD are depicted. Notice that there is a characteristic sharp dip (in Fig. 11a) at 330°C in the DTA record and apparently no change in the DSD spectrogram curve of Figure 11b below 300°C. Actually, there are several fascinating very low loss changes that occur in the dielectric record below this temperature. For example, Krum and Mueller⁴ made a series of dielectric measurements on PTFE ranging from amorphous to crystalline conditions

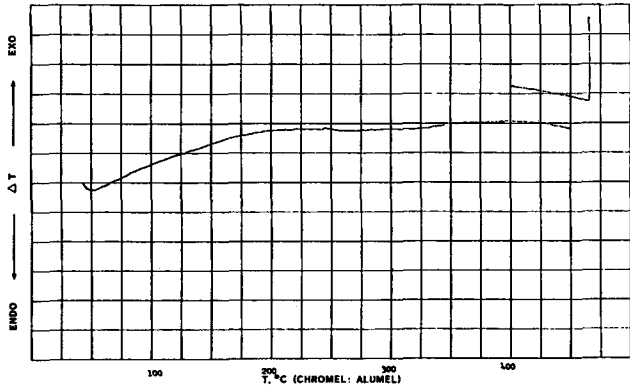


(a)

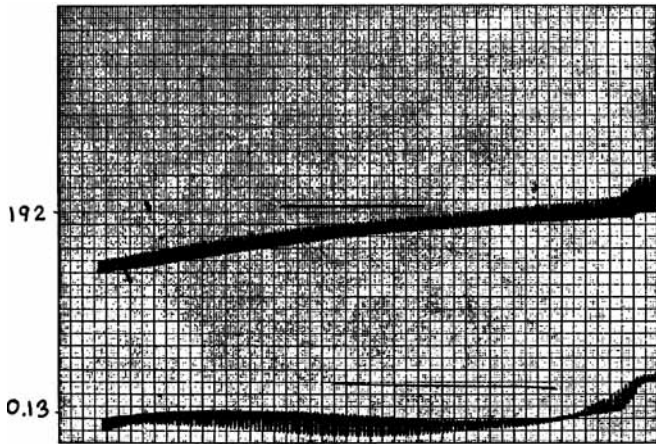
Fig. 13. (continued)



(b)



(c)



(d)

Fig. 13. Changes of boron nitride as seen in the DTA and dielectric DSD record after thermal cycling to 500°C.

and found several characteristic reference peaks—alpha, beta, and gamma. Alpha is believed to be associated with the amorphous regions and beta with the crystalline regions, while the gamma relaxation results from the limited motions of short-chain segments, as in a crank shaft or local mode type of relaxation. It seems probable from dielectric E_a calculations that the beta mechanism involves torsional oscillations of chain segments around the chain axis within the crystal and that the alpha process is related to large-scale backbone motions characteristic of a glass transition.

Polyimide resins have been studied extensively by Wrasidlo² and at Tetrahedron⁵ during cure as well as in the cured state, using simultaneous DTA and dielectric measurements, occasionally correlated against other forms of thermal analysis such as birefringence thermal analysis, mechanical modulus thermal analysis, and several others. For brevity, only three are considered here: DTA and dielectric properties, determined simultaneously, and dynamic mechanical properties, determined with a direct-reading commercial viscoelastometer (Vibron VDV II).

In Figure 12, a method of measurement previously described, that of the circle loop, is shown for a polyimide resin, with characteristic changes noted on the graph. The processing of polyimide materials into finished articles requires a very critical control over the curing process and particularly of the point of pressure application. The resin must be sufficiently gelled so that, upon application of pressure, it will neither be excluded from the parts, leaving it resin starved, nor overcured, which would produce a void-ridden and improperly consolidated finished part. Notice the arrow which is pointing toward a dip in the curve. This is a point for pressure application, being between the transition from a gelled to a hardened condition. The exact point for pressure application is affected by other factors, such as the amount of pressure applied. For example, with higher pressures, we can within limits delay its application. So, although the dielectric record does not give us an absolute point for taking action, it does give us a reference and a reliable indication of resin condition, facilitating process control.

Although we have so far discussed only simultaneous dielectric and DTA measurements on polymeric materials, any dielectric material, organic or inorganic, may be similarly studied. As an example, note that in our simultaneous measurements of boron nitride (DSD and DTA), irreversible transitions occurred on the first cycle using fresh material both in the DTA and the dielectric curves (Fig. 13).

APPLICATIONS

Simultaneous dielectric-DTA analyses are being used in many areas of research and industry. For example, a circuit board manufacturer reports a reduction in his scrap from 25% to 0. Studies of radiation-cured resin systems are being made. A commercial aircraft corporation is using simultaneous dielectric-DTA measurements to determine that all outgoing materials have been fully cured. Primer and toothpaste tube

coatings are being evaluated. Dielectric analysis replaced NMR and GC in one operation as a process control tool after its results were correlated with those obtained from the previously used instruments. Incoming inspection for tank car lots of polymers such as MMA have been greatly improved. The cook of resins has been followed through dielectric analysis. Routine structure analysis has been performed and the structure of polymeric systems is being determined through the results of various simultaneous dielectric-DTA measurements.

SUMMARY

Dielectric methods of analysis, by themselves and coupled with other techniques such as DTA, yield insights into the microscopic structure of organic and inorganic materials. The simplicity of dielectric measurement techniques and the nonobtrusive character of the dielectric dipole used as an internal sensor provides a method of analysis which lends itself to cross-checking against the findings of other measurement methods such as DTA. Results of these cross-checks yield insights into the internal structure of organic and inorganic dielectric materials which often have broad practical utility. This is a pioneering area in which there is a need for much further work—in the investigation of biological polymer structure, viscoelastic behavior, and the polymer curing and degradation process and the development of continuous methods for industrial process control. We hope that this paper will stimulate increasing interest in this subject.

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