

# Coatings Characterization by Thermal Analysis

by C. Michael Neag<sup>1</sup>

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American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959

THERMAL ANALYSIS (TA) ENCOMPASSES A VARIETY of techniques used to measure changes in material properties with changes in temperature. These techniques apply broadly in materials science and find use in characterizing liquids, polymers, and inorganic materials. The many results obtained using TA fit neatly into Van Krevlan's [1] classification of material properties. He divides material properties into three distinct but interrelated categories: (1) intrinsic properties, (2) processing properties, and (3) product or article properties. Intrinsic properties such as the glass transition temperature ( $T_g$ ) or elastic modulus arise from the chemical and physical structure of a material, can be measured with precision, and may form the basis for predictive empirical relationships. A material's process properties depend on the interplay of intrinsic properties and process conditions (e.g., synthesis temperature or mixing time). In essence, they reflect a material's intrinsic properties in a dynamic environment. In practice, the interaction of a material's intrinsic properties and process properties yield a unique product embodying still different properties. Unfortunately, the relationship between intrinsic properties and process properties is poorly understood, difficult to measure, and more difficult to predict. Because product properties depend on this ill-defined relationship, their meaning becomes quite subjective. Simply put, a paint made and applied one day may behave quite differently than a paint made and applied another day, and the reasons for the observed differences often remain obscure.

Thermal analytical techniques provide tools to help clarify these hard-to-understand relationships, helping to reduce product development time and manufacturing costs, while shaping the best possible product. The instrumentation supporting thermal analysis has grown remarkably in both versatility and sophistication: automated systems, absolute control of applied stresses, and tenth-of-a-degree temperature resolution have replaced strip chart recorders, spring-loaded stresses, and "give or take a degree" temperature resolution.

The advent of the inexpensive microprocessor chip probably represents the most significant step in the development of improved commercial thermal analyzers. The development of powerful PC and microcomputer-based controllers have dramatically simplified experimental procedures, data collection, and data analysis in thermal analysis. In general, automating these instruments has dramatically improved the experimenter's control over the sample environment. These

improvements allow technologists to complete complex experiments involving multistep heating programs and several purge gases. At the same time, calibration routines were also simplified and the accuracy and precision of the results improved. All of these advances came with the additional benefit of unattended operation. In fact, several commercial suppliers offer instruments with robotic control that permit the analysis of scores of samples at the touch of a button.

The simple yet highly sophisticated character of these instruments has a major drawback: their simplicity significantly increases the potential for misinterpreting experimental results. With advances in automation, thermal analytical techniques have moved closer to simple "turn-key" operations and have reduced considerably the technical demands on the user. TA has become a marvelously simple process that unfortunately requires little understanding of the instrumentation or the results. A few minutes in sample preparation yields a raft of data from sophisticated data analysis software, considerably increasing the potential for error in data interpretation or analysis. The improvements in instrumentation and software demand greater caution from the scientist in experimental design and results interpretation. Wendlandt [2] and Earnest [3] discuss the advent of automation in thermal analysis, and two volumes edited by T. Provder [4,5] describe laboratory automation and computer applications in polymer science more generally.

## Coatings and TA

In the coatings industry—limited here to commercial paints and industrial coatings—TA has proven to be a cost effective means for understanding the interrelationship between a coating's synthesis, formulation, and end-use performance [6]. Techniques historically important in coatings characterization can be broadly grouped under the headings of differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermomechanical analysis (TMA), dynamic mechanical analysis (DMA) and thermogravimetry (TG). Techniques such as dielectric analysis (DEA) and evolved gas analysis (EGA) have gained popularity as tools for coatings characterization as well. Although results are easily obtained using these techniques, they are grounded in complex thermodynamic and kinetic principles. Excellent overviews of the foundations, instrumentation, and applications of thermal analysis can be found in reviews by Wendlandt [2], Wunderlich [7], and Turi [8,9]. The International Confederation for Thermal Analysis (ICTAC) also provides an overview of TA and a list of reference articles [56].

<sup>1</sup>Associate scientist, The Glidden Company, a part of ICI Paints World Group, Glidden Research Center, 16651 Sprague Road, Strongsville, OH 44136.

While a single TA technique may adequately characterize a research or production problem for a given system, questions often arise in the coatings industry that require several analytical techniques for adequate characterization. In fact, relying on a single characterization method could lead to serious errors in interpretation and, depending on the problem, serious financial consequences as well. The continuing development of simultaneous methods in TA underscores the value of combining techniques. They offer the advantage of simultaneous analysis of changes in physical and/or chemical properties under identical thermal conditions. There are a variety of these instruments available: examples of these "hyphenated" techniques include TG-MS (mass spectrophotometry), TG-DTA or TG/FT-IR (Fourier transform infrared spectroscopy).

Industrial applications of thermal analysis for coating characterization fall loosely into four areas:

- Product research and development.
- Problem solving.
- Quality control and quality assurance.
- Competitor products analysis.

While the results obtained using thermal analysis often focus on intrinsic properties such as component Tg's or the complex analysis of a material's viscoelastic behavior, thermal analytical methods are more typically focused on process properties and product properties. This paper provides an overview of the use of TA in the coatings industry and includes descriptions of the instrumentation, experimental conditions, and typical results.

## EXPERIMENTAL TECHNIQUES

Scans were made using the TA Instruments' (formerly DuPont) 990, 9900, 2000, or 2100 temperature programmer controller. Nonisothermal studies were completed at heating rates varying from 5 to 15°C/min; isothermal temperatures will be noted as required. All scans were made under dry nitrogen or air. Each instrument was calibrated and operated using the manufacturer's recommended procedures. The typical operating conditions for each instrument are described below, with other important key experimental variables noted where necessary. A general overview of running experiments with each instrument is included at the end of each section.

**DSC**—Nonisothermal scans were made variously using the TA Instruments' 910 and 2910 DSCs, typically with 5.0 ± 0.1-mg samples. Materials were usually scanned twice, initially to establish uniform thermal histories and again to learn about specific physical properties. Runs were generally made at heating rates of 15°C/min between -125° and 250°C under a 50 mL/min nitrogen or air purge. In some instances, latex samples were introduced into liquid drop pans and dried in a controlled humidity chamber for a minimum of 24 h before analysis.

**DSC Reaction Kinetics**—Similar conditions to those described above were used, although heating rates were generally held to about 5°C per minute. Samples of unreacted material weighing about 10 mg were placed in special pans for liquid samples. In the residual heats of reaction experi-

ments, heats of reaction were determined for samples removed from a batch reactor at 10-min intervals throughout the reaction process. The residual heats were measured under nonisothermal conditions using commercially available software. The ratio of partial heats of reaction to total heat of reaction as the polymerization progressed was given as the percent chemical conversion.

**DMA**—DMA scans were made variously in vertical and horizontal modes on TA Instruments' 981, 982, and 983 DMAs. All studies were completed at 5°C/min, usually under nitrogen purge. Cure studies employed either fiberglass braid supplied by TA Instruments or stainless steel mesh (Cleveland Wire Cloth & Mfg., Cleveland, OH). In cure studies, 100-μL wet samples were applied to substrates mounted in the DMA using analytical pipettes [50 mL ± 0.5% to deliver (TD)]. Isothermal temperatures were typically attained by mimicking the come-up time in an oven. For example, if a coated panel required 4 min to reach bake temperature in a production scale oven, then a similar time schedule was programmed into the DMA.

**TMA**—Thermomechanical and dilatometric experiments were made using TA Instruments' 942 and 943 TMAs. Scans were made at 5°C/min under nitrogen or air between about -50 and 250°C. In general, the sample was cooled at least 50°C below the expected transition temperature. TMA scans were typically made directly on coated substrates, while dilatometric experiments were completed on samples varying between 0.1 and 0.6 mm in thickness. In the penetration experiments, loads were typically about 5 g (0.05 N).

**DEA**—The TA Instruments' 2970 DEA and either the parallel plate or ceramic single surface sensors were used in the dielectric experiments. Parallel plate sensors were used to study thin films removed from various substrates. Ram force varied from a few newtons to 175 N depending on the coating. The ceramic single-surface sensor was used to study resins and powders. 100-μL samples were spread uniformly on the sensor and dielectric measurements recorded from 0.1 Hz through 100 kHz in order-of-magnitude increments. Heating rates were selected to ensure that an entire set of frequencies (0.1 Hz through 100 kHz) could be recorded for each 1°C increase in the sample temperature. Samples were typically scanned at 1 to 2°C/min between -125 and 200°C under nitrogen.

**TGA**—TA Instruments' 950, 951, and 2950 TGAs were used in the examples described here. Samples used in typical thermogravimetric experiments usually weighed between 3 and 10 mg. Scans were made at 10°C/min under nitrogen beginning at room temperature (RT) and ending at 600°C. The high-resolution thermogravimetric analysis described here was completed at 50°C/min in nitrogen at a resolution factor of 5; sample weights ranged between roughly 10 and 12 mg.

## DIFFERENTIAL SCANNING CALORIMETRY

In differential scanning calorimetry (DSC), the difference in heat flow between a sample and a reference is measured under precisely controlled thermal conditions. Coatings generally possess one or more characteristic transitions, includ-

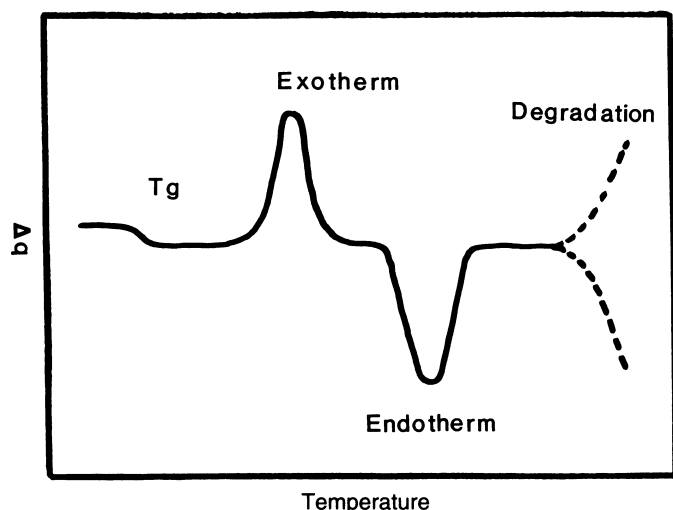


FIG. 1—Schematic DSC curve illustrating common transitions observed by DSC ( $\Delta q$  = heat flow).

ing (1) the glass transition ( $T_g$ ) or a transition related to changes in specific heat; (2) exothermic peaks brought about by a physical process or a chemical reaction such as crystallization or a chemical process such as a cross-linking reaction; (3) narrow endothermic peaks related to fusion or melting; (4) broader endothermic peaks caused by the volatilization of low-molecular-weight materials, dissociation, or decomposition; and finally, (5) an increase or decrease in heat flow with oxidative or thermal decomposition. The results shown in Fig. 1 illustrate most of the transitions common in coatings. The DSC has a number of important uses in coatings characterization; two of the most important— $T_g$  determination and reaction kinetics analysis—are described in more detail below.

**Glass Transition Temperatures**—Probably the best understood and most commonly used property of polymers, glass transition temperatures are important in virtually every phase of a coating's development and manufacture. The  $T_g$  marks a polymer's transition from an amorphous glass to a rubbery solid and defines the limits of processability for most polymers. In a nonisothermal or rising temperature DSC experiment, the glass transition coincides with a relatively sharp increase in heat flow to the polymer and a corresponding increase in the polymer's specific heat. Several techniques can be used in the assignment of a DSC  $T_g$ , including the onset, midpoint, and endpoint of the transition; in practice, the  $T_g$  is most commonly assigned to the extrapolated onset of the transition.

**Sample Preparation and  $T_g$  Measurement**—Measuring the glass transition temperature usually means nothing more than removing a sample from a substrate, placing it in a sample pan, and heating through the glass transition temperature in the DSC. Either of two techniques can be used to determine the  $T_g$ . When the "product"  $T_g$  (including all processing and thermal history effects) is of interest,  $T_g$ 's are obtained with a single temperature sweep. Where thermal history effects are unwanted complicating factors, two temperature sweeps are used. The first sweep removes thermal history effects (for example, sample preparation or aging

effects) while the second sweep gives the  $T_g$ . The latter technique works very well provided that there are no chemical changes, solvent losses, or morphological alterations during the first sweep.

Sometimes, inconsistencies in sample preparation or a seemingly unimportant detail can significantly influence the interpretation of the results—particularly when first run transitions are required. In the example below, two latexes—one scraped from a glass slide and placed in a vented pan and the other dried directly in a liquid drop pan—produced considerably different results. The samples were dried side by side in a desiccator before analysis.

The sample scraped from the glass slide shown in Fig. 2 exhibits a large endothermic peak centered around 75°C. Normally, this endotherm would suggest the loss of a volatile component or an important morphological feature. However, the results for the latex dried directly in the liquid drop pan suggest that something else is influencing the results. The heat flow curve for the latter sample exhibits no endotherm and has a  $T_g$  some 15°C higher than the sample removed from the glass slide. High-resolution videography resolved the issue, showing that the difference in  $T_g$  and the endothermic "event" was probably brought about by the softening and subsequent relaxation of the latex pieces scraped from the glass slide. What appeared as a significant morphological feature was nothing more than an artifact of the sample preparation process. In a typical two-sweep  $T_g$  measurement, this endotherm most likely would have been ignored and only the second run  $T_g$  reported, but, in studies that require the first-run data (as was the case here), the wrong conclusions could have been drawn.

**$T_g$  and Composition**— $T_g$ 's obtained by DSC are also used to confirm the accuracy of  $T_g$ 's calculated from additive relationships like the Fox equation [10]. The Fox equation and others like it are employed by coatings chemists in synthesizing copolymers to a specific  $T_g$ .  $T_g$ 's obtained with these equations are based on the interrelationship of the molar or weight fraction of each monomer and their corresponding  $T_g$ 's. While experimental results usually confirm the accuracy of  $T_g$ 's calculated with these relationships, experimental and calculated results can deviate significantly from one another, a fact that underscores the need to verify expected results with an objective measure.

The discrepancy between calculated and experimentally obtained  $T_g$ 's for four acrylic copolymers, shown in Fig. 3 and Table 1, aptly demonstrate the importance of corroborating calculated  $T_g$ 's by DSC. In this example, the  $T_g$ 's determined by DSC are much lower than the  $T_g$ 's obtained using the Fox equation. Close examination of the DSC heat flow curves gives outstanding clues about the character of the polymers being analyzed. Compared to a typical  $T_g$ , the transitions in Fig. 3 are very broad—covering some 40 to 50°C—and quite shallow, falling less than 0.1 cal/s/g from beginning to end. The character of the glass transition region in a typical DSC is quite different. The temperature range of this region is usually no more than about 25°C wide and usually drops more than 0.5 cal/s/g over the  $T_g$  range. The differences between assigned and calculated  $T_g$ 's probably stem from the combined effects of monomer sequence distribution [11] and end group effects related to the relatively low molecular weight

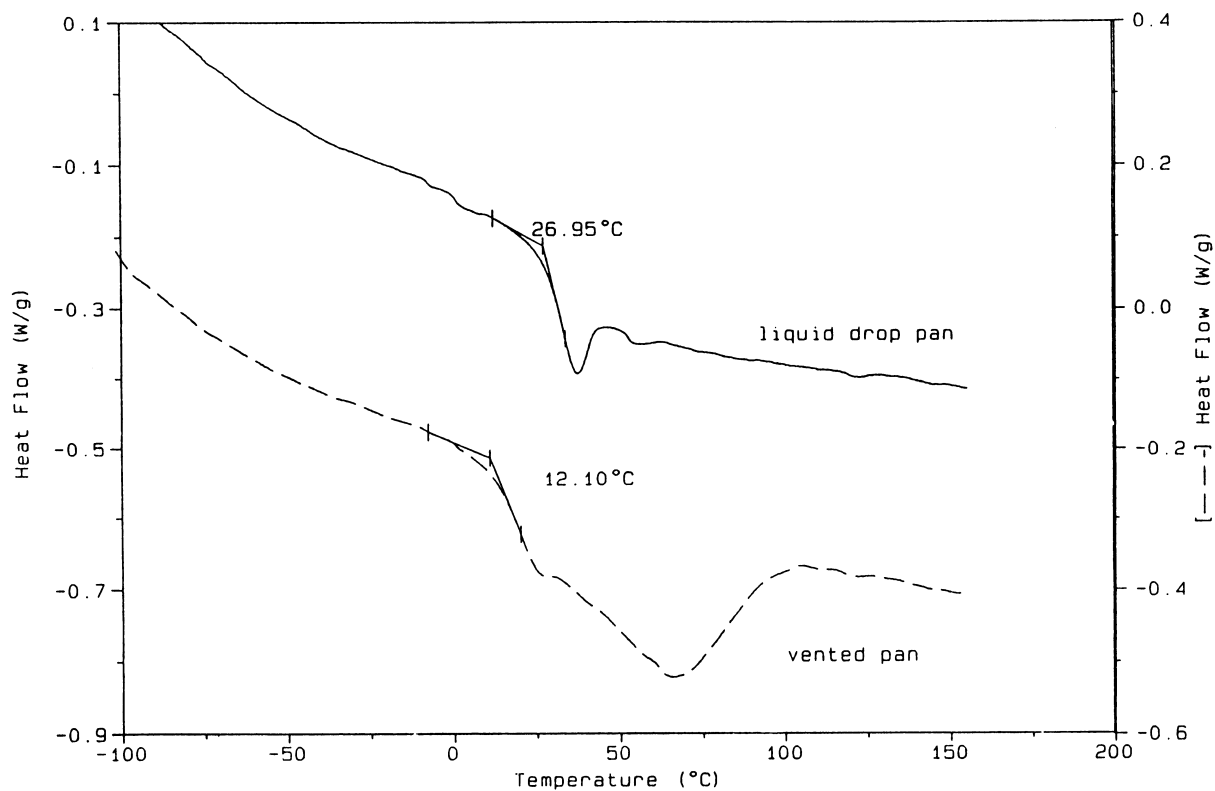


FIG. 2—Characteristics of the glass transition in identical latexes prepared by different methods.

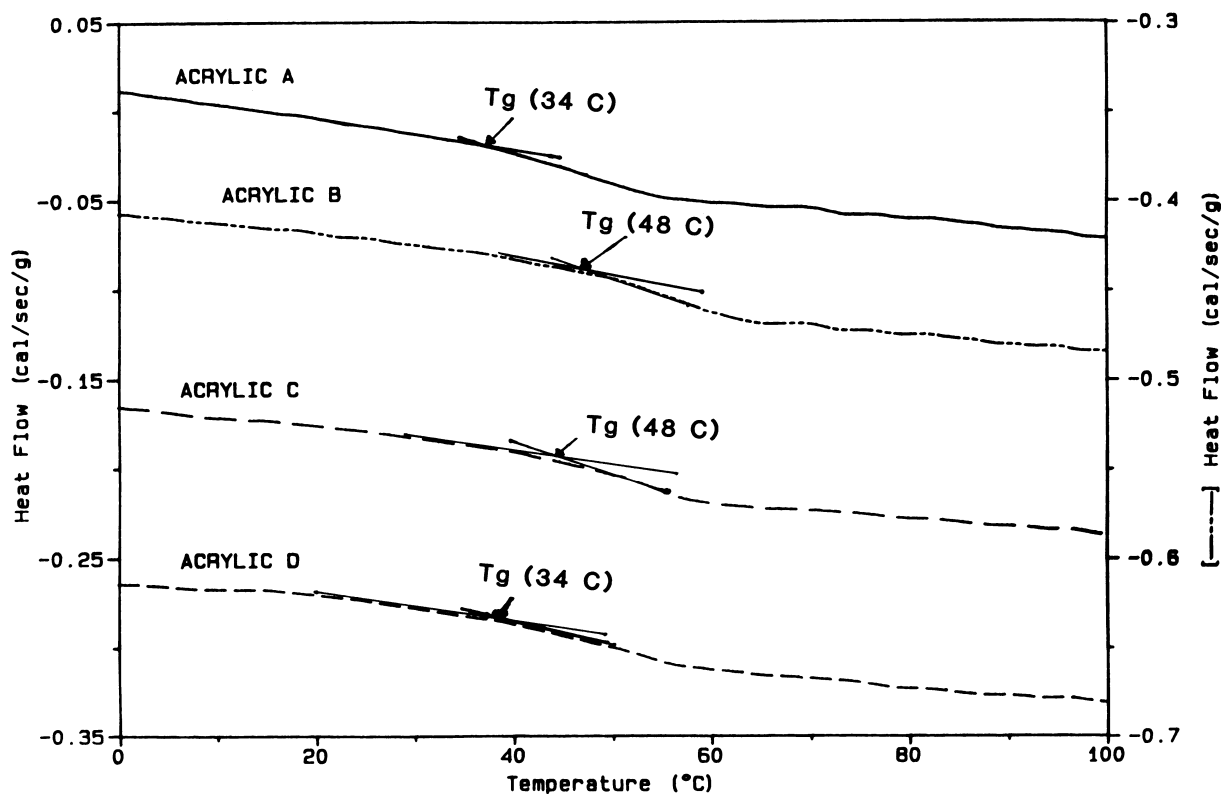


FIG. 3—Glass transition temperatures for four acrylic copolymers.

**TABLE 1**—Calculated<sup>a</sup> and experimentally (DSC) determined Tg's (°C) for four acrylic copolymers.

Acrylic Copolymer	DSC Tg	Fox Tg
A	34	60
B	48	65
C	48	70
D	34	75

<sup>a</sup>Tg's were calculated using the Fox equation.

[12] of these copolymers. The polymers used in this experiment were all low-molecular-weight tetramers (number average molecular weight < 5000) composed of various combinations of methylated and butylated acrylics. Van Krevlan [1] provides a more comprehensive overview of polymer properties which could have an influence on the assignment of the glass transition temperature.

## REACTION KINETICS

A number of techniques have been developed for measuring the kinetic parameters of chemical reactions from DSC data. The primary advantage of these techniques over traditional wet chemical techniques is their speed and simplicity. Research in reaction kinetics analysis by DSC includes studies focused on isothermal techniques [13–15], nonisothermal (also known as temperature variant, rising temperature) or dynamic methods [16–17] and multiple scan methods [18–19]. Each method uses the rate of heat evolution as the computational parameter, implicitly assuming that the reaction is not autocatalytic, has one rate-limiting step, and is unaffected by changes in reactant concentration or volume. The validity of kinetic data obtained using nonisothermal procedures has been the source of considerable technical effort and discussion in the literature (see, for example, Refs 20 and 21).

Nonisothermal reaction kinetics analysis plays an important role in the characterization of coatings. Differential methods based on the work of Borchardt and Daniels [16] are the most commonly used in obtaining reaction kinetics parameters by DSC. These methods assume that the heat evolved during a reaction is proportional to the extent of reaction. The order of reaction,  $n$ , the activation energy,  $E$  (kJ/mol), and the Arrhenius constant,  $A$  (s<sup>-1</sup>), are determined using an equation based on a general  $n$ th order rate expression

$$\frac{dF(t,T)}{dt} = k[1 - F(t,T)]^n \quad (1)$$

where  $F(t,T)$  is the fractional extent of conversion [partial heat of reaction  $\Delta H(t,T)$  divided by the total heat of reaction  $H_0$ ],  $k$  is the rate constant,  $t$  is time, and  $T$  (K) is the absolute temperature. The temperature dependence of the rate constant is given by the Arrhenius expression

$$k = A \exp(-E/RT) \quad (2)$$

where  $R$  is the ideal gas constant (J/mol K). The methods used here have been described in detail elsewhere [22–23].

In nonisothermal kinetics experiments, autocatalytic reactions and first-order reactions are virtually indistinguishable

because both reactions produce a uniform, monomodal, exothermic peak as the experimental temperature increases. The only way to determine the nature of the reaction mechanism is by running an isothermal experiment. An isothermal experiment will clearly differentiate between the two reaction types because the exothermic peak marking the maximum rate of reaction will occur at very different points, depending on the nature of the reaction. In a reaction that obeys first-order kinetics, this peak will occur immediately after reaching the isothermal temperature. In an autocatalytic reaction, the maximum rate of reaction—and therefore the peak maximum—occurs well after reaching the isothermal temperature.

## Epoxy-Amine Reaction Kinetics

Maximizing the efficiency of a reactor and minimizing raw material waste in a chemical reaction depends inherently on knowing how a reaction proceeds and, more specifically, how long the reaction takes to reach completion. Unfortunately, measuring the rate and degree of conversion in reactors holding hundreds or even thousands of gallons is a prohibitively expensive process during product scale-up. Small-scale laboratory DSC experiments representative of a production reaction can significantly reduce reactor time and process costs. Modeling the extent of reaction using DSC kinetics analysis can further shorten the development process and can be used to predict the extent of reaction under widely varying temperatures and reaction times. In the example that follows, these techniques were used to optimize reactor time and improve productivity in manufacturing. The reaction involved a typical diglycidyl ether of bisphenol A (DGEBA) epoxy and an amine.

In this example, chemists arbitrarily placed the time to form an epoxy adduct at 8 h, a substantial manufacturing cost when considering reactor time and labor. However, predictions based on nonisothermal DSC reaction kinetics showed that the reaction should actually reach completion much faster than 8 h. In fact, DSC reaction kinetics parameters ( $n = 1.1$ ,  $E = 72.0$  J/mol, and  $\ln A = 19.2$ ) indicated that the process should take about 2 h under the specified polymerization conditions. These results were then corroborated by measuring the residual heats of reaction (see experimental for details) observed in small samples taken from a 100-gal reactor. Figure 4 compares predicted conversion with the residual heats of reaction measurements. While neither method was extended to show the actual time required to reach 100% conversion, extrapolation to 100% conversion indicates the reaction should reach completion after about 2 h. Table 2 compares selected data from Fig. 4 at specific reactor times. These results show that the reaction reached a higher level of conversion (based on DSC residual heats) in the manufacturing process (88%) than predicted by DSC (67%). Nonetheless, the extrapolated end-point from the DSC kinetics analysis—although a bit high at 2.5 h—is much better than the 8-h reactor time set arbitrarily by the chemists.

The discrepancies between the measured and calculated degrees of conversion are probably related to competing side reactions that could occur in DSC experiments (i.e., at elevated temperatures) but not during manufacturing and also to the vast difference in the reaction conditions: DSC kinetics

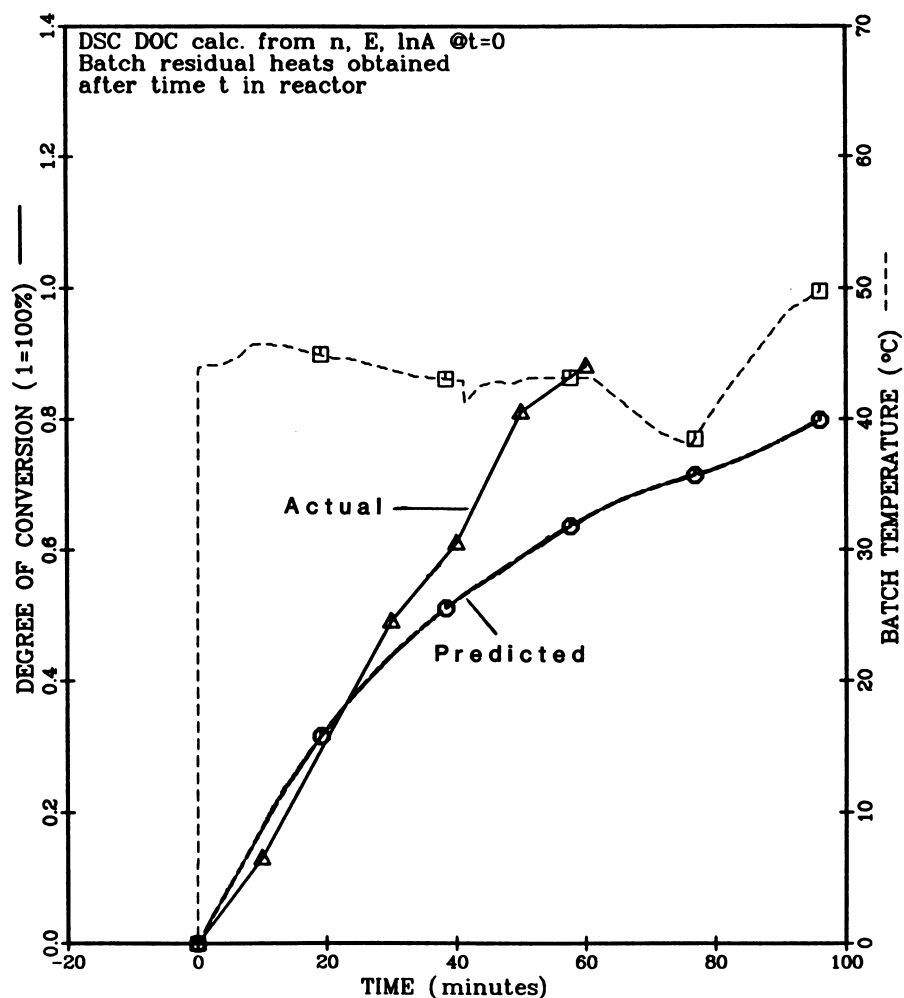


FIG. 4—A comparison of actual and predicted degree of conversion in an epoxy-amine reaction. The predicted degree of conversion at each point was based on DSC kinetics analysis, while the actual degree of conversion at each point was based on the residual heat of reaction on samples removed from the reactor.

analyses were made using fresh 5-mg samples, while the residual heat studies were made with samples taken from a 100-gal reactor.

### Coatings Characterization by DSC

**Sample Preparation:** The materials typically analyzed in the coatings industry can come as either solids or liquids. Solids require little special preparation; they just need to fit in

TABLE 2—Chemical conversion obtained from residual heats of reaction and simulations using DSC kinetics parameters.

Reaction Time, min	Actual % Conversion	Predicted % Conversion
0	0	...
10	14	19
20	31	33
30	49	43
40	61	53
50	81	61
60	88	67

the pan and, most importantly, remain very flat on the bottom of the pan. Liquids are another matter and usually require a special container for analysis. No matter what the form, limit your sample size to somewhere between 5 and 10 mg. Large samples (>10 mg) may not heat uniformly, with the outer layers heating more rapidly than the center of the sample. You can also get results with samples in the 1-mg range, but using smaller masses can reduce resolution. For a more accurate assignment of the  $T_g$ , use high sample weights (ca. 20 mg) and slow heating rates (1°C/min).

Either open or closed pans can be used. We prefer closed pans with perforated (use a fine needle) lids. Lids help keep the DSC oven or cell clean; the perforations prevent pressure buildup caused by solvents or low-molecular-weight reaction products. Many others use only open pans.

Liquid paint and latex samples are treated somewhat differently in that they are placed in open pans (especially designed for liquids) and allowed to dry (24 h minimum) before analysis. This approach prevents the development of artifacts that sometimes occur when a dried sample is scraped from a substrate and placed in the pan.

**Purge gas:** The selection of purge gas depends on your objectives. High-purity dry nitrogen (99.99%) is typically used. It offers low cost and reasonably good heat transfer. Argon, another frequently used gas, improves heat transfer and the resolution of the analysis but at increased cost. Purge rates vary with the instrument.

**Temperature Range and Heating Rate ( $\beta$ ):** Start each temperature sweep at about  $-125^{\circ}\text{C}$  and end at least  $50^{\circ}\text{C}$  above the  $T_g$ . This temperature range will include any transitions in typical coating systems that could affect performance. If you know the  $T_g$  of your sample and you are unconcerned about ancillary transitions, use the 50/50 rule: start runs  $50^{\circ}\text{C}$  below the  $T_g$  and end them at least  $50^{\circ}\text{C}$  above the  $T_g$ , making sure that the sample has time to equilibrate at the starting temperature.

The important consideration in selecting a heating rate is heat transfer and the steady state conditions in the sample. For routine analysis, a  $15^{\circ}\text{C}/\text{min}$  heating rate offers a good compromise between run time and resolution. Keep in mind that high heating rates can produce thermal lag in the sample and tend to broaden transitions. And, when there are two or more transitions, they tend to run together. Slower heating rates are usually used where there is a need for high resolution. But, when time is not a concern, slower rates are always preferable. There are also instances, for example film formation experiments, where isothermal temperatures are necessary. Choose an experimental temperature slightly higher than ambient, say  $30^{\circ}\text{C}$ , for controlled room temperature experiments.

**Thermal History:** In most analyses, the sample should be analyzed twice. In unreactive systems, the first sweep erases any effects of the sample's previous thermal history and establishes a uniform baseline for each sample—this is especially important in comparing a series of samples.

In reactive materials, analyze through the cure temperature and allow for the reaction to reach completion. Determining the proper temperature range may require some "scouting" experiments. In isothermal cure studies at elevated temperatures, try to simulate bake conditions. Select an initial heating rate that approximates come-up time for a substrate in an oven and add enough time at the bake temperature to match the typical oven "dwell" time.

**Data Collection:** In non-isothermal or rising temperature experiments, try to average between two and eight data points per degree Celsius increase, depending on the experimental objectives. Higher heating rates require higher data-collection rates to obtain the same resolution. Note that high data-collection rates at slow heating rates can produce large data files. Data collection for isothermal studies must be tuned to the time required for an event to occur. Fast events would require high data collection rates; slower events would require correspondingly lower rates.

## DYNAMIC MECHANICAL ANALYSIS

DMA measures the viscoelastic response of a material under a periodic load. Dynamic mechanical analysis represents one of several methods for mechanical properties analysis [24–26] providing a valuable link between chemistry, morphology, and performance properties [27–29]. The DMA's applications range from the measurement of bulk viscoelastic properties to the sophisticated analysis of the kinetics of the

cross-linking reaction. Depending on the geometry of the clamps and the instrument's design, the oscillatory load applied may be in flexure, tension, compression, or torsion; sample oscillation may be either at resonant frequency or at fixed frequency. These tests simultaneously produce elastic modulus and mechanical loss or damping values. Modulus values (flex, Young's, shear, bulk) provide an indication of material stiffness, while mechanical damping correlates with the amount of energy dissipated as heat during the deformation of the material. In tensile mode, these instruments can provide creep and stress relaxation data and can even be used in WLF [30] transformations (see Ref 30).

In the coatings industry, DMA is broadly applicable to the study of film properties [31] and particularly important for cure process studies [32–34]. Another important application of the instrument involves characterizing paints after application and the film-formation process. A detailed overview of the use of DMA in thermoset cure studies is provided later in the chapter. Figure 5 illustrates the typical viscoelastic response for a generalized polymer coating. In this example, the glass transition temperature corresponds to a large decrease in modulus beginning near  $25^{\circ}\text{C}$  and a peak centered at about  $70^{\circ}\text{C}$  on the loss modulus curve. In noncrystalline polymers, transitions found below the  $T_g$  or in the glassy state are usually associated with the molecular motion of the backbone or small groups pendant to the main chain. At the same time, modulus values in the region above the  $T_g$ —the rubbery state modulus—impart information about a material's molecular weight or degree of cure, depending on the material. In thermoplastic materials, increasing rubbery state modulus values usually indicates increasing molecular weight. In thermoset materials, increasing rubbery state modulus values indicates higher cross-link density. A more complete description of the dynamic mechanical properties can be found in monographs by Nielsen [24,25] and Ward [26].

## Synthetic Variables and Morphological Character

One of the strengths of dynamic mechanical analysis lies in its utility for resolving the effects of relatively minor changes in formulation or processing. Differences in these variables (usually) induce easily discernable changes in the viscoelastic properties of a polymer. For example, the materials shown in Figs. 6A and 6B are both epoxy acrylic coatings used in food packaging. While the coatings are made of virtually the same materials, their chemistries and processing conditions are different.

The presence of two glass transitions in the relative modulus curves in these graphs indicates that both coatings are heterogeneous systems. However, these curves give little indication as to whether the epoxy or the acrylic is the continuous phase. A comparison of the damping peaks reveals a difference in the peak intensity (or peak height) of the two transition regions. In filled systems, polyblends, and grafted systems, the intensity of the damping peak gives a rough estimate of the concentration of the components and an indication of which phase is continuous. The greater the concentration, the larger the damping peak and the more likely that phase is continuous [24]. In Fig. 6A, the epoxy phase peak at roughly  $130^{\circ}\text{C}$  has considerably greater magnitude than the

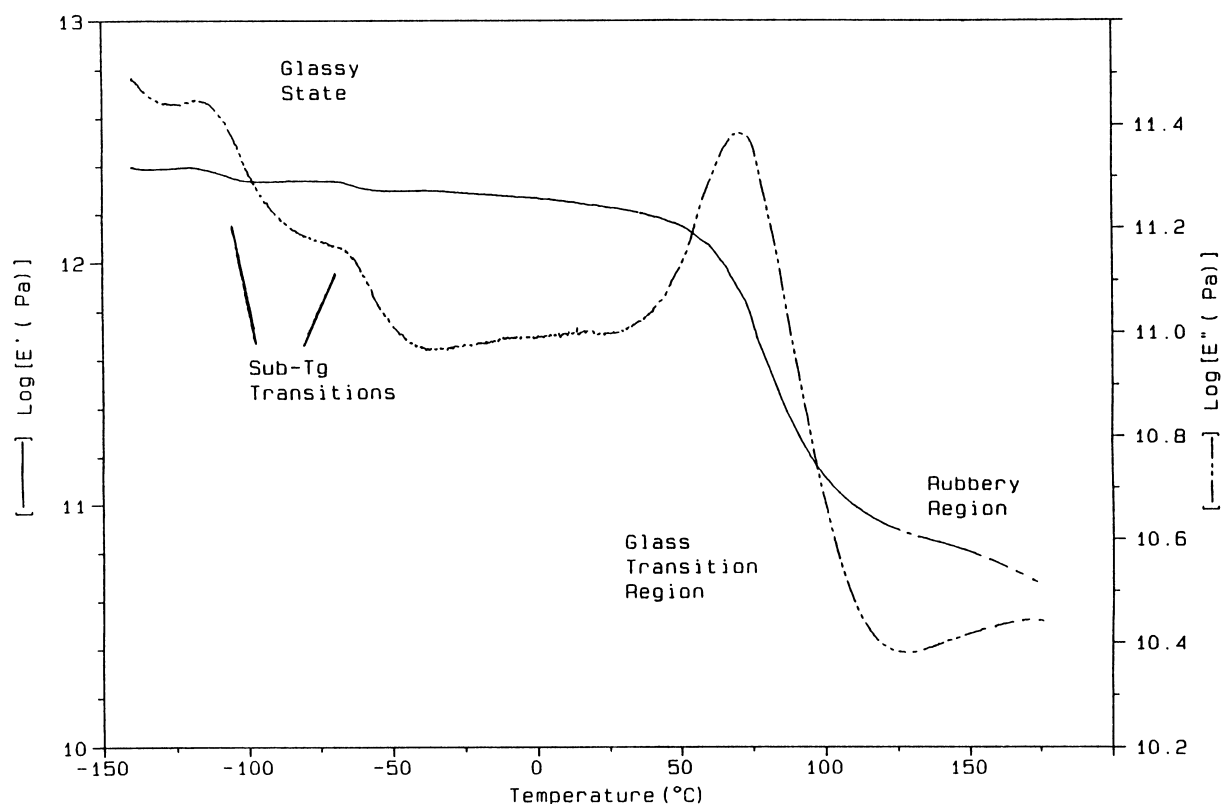


FIG. 5—Typical viscoelastic response in polymeric systems, log relative modulus ( $E'$ ) and log relative loss (damping,  $E''$ ).

one assigned to the acrylic and so would be the continuous phase. In Fig. 6B, the opposite is true. In this case, the acrylic phase centered near 90°C is continuous while the epoxy is the dispersed phase.

Aside from the information on morphology, these curves also give us information on the relative miscibility of these systems. If these two polymers were totally miscible, both the modulus and damping curves would have only one transition. Since there are two, it is clearly a two-phase system. Careful scrutiny of the two systems reveals that the peaks in Fig. 6B fall much closer together than those in Fig. 6A. This strongly suggests that the conditions used to produce the material in Fig. 6B produce a more miscible polymer.

### Coatings Characterization by DMA

Dynamic mechanical analysis can be one of the most demanding and least forgiving of all the TA techniques. It's vitally important to spend time learning the instrument's idiosyncrasies before putting complete faith in the viscoelastic measurements the instrument produces. Each commercial instrument offers unique sample mounting geometries and usually offers a variety of experimental approaches. Regardless of the experimental approach, take the time to run a half-dozen experiments using identical experimental conditions so that you can better understand the range of results to expect under a given set of experimental conditions.

**Sample Preparation:** There are several approaches to forming free films for DMA investigations. These include coating low-energy surfaces like PTFE (Teflon) or polypropyl-

ene or coating thin aluminum sheet stock, allowing sufficient time for film formation, and dissolving the aluminum away with an alkali. Sample dimensions must always conform to the limits prescribed by the instrument manufacturer; wherever possible, however, sample thickness should closely approximate the thickness of the coating film in the field. In this way, test results will more closely represent those found in realistic end-use conditions.

Unfortunately, free films are not always a viable experimental choice. In those instances, coated substrates, e.g. very thin stainless steel shim or fiberglass braid, are often used. Although constitutive equations are available for obtaining absolute mechanical properties values from coated substrates, usually only relative measurements are made using this approach.

To insure uniform thermal histories, prepare specimens in a controlled environment. Small differences in film-forming temperature or humidity in replicate runs on the same coating can make it appear as if two different coatings had been tested. Well-controlled and consistent sample preparation allows the additional advantage of comparing results from tests made over many months or years without concern about differences in film-forming conditions.

**Heating Rate:** Undoubtedly, one of the most, if not the most, important consideration is choosing proper heating rates. While most instruments make rapid heating rates available (some manufacturers claim 200°C/min), it is wisest to choose very slow heating rates—at most, heating rates of about 1 or 2°C/min. Slow heating rates allow the entire sample to equilibrate to temperature change and thereby improve the reliability of transition temperature assignments. When



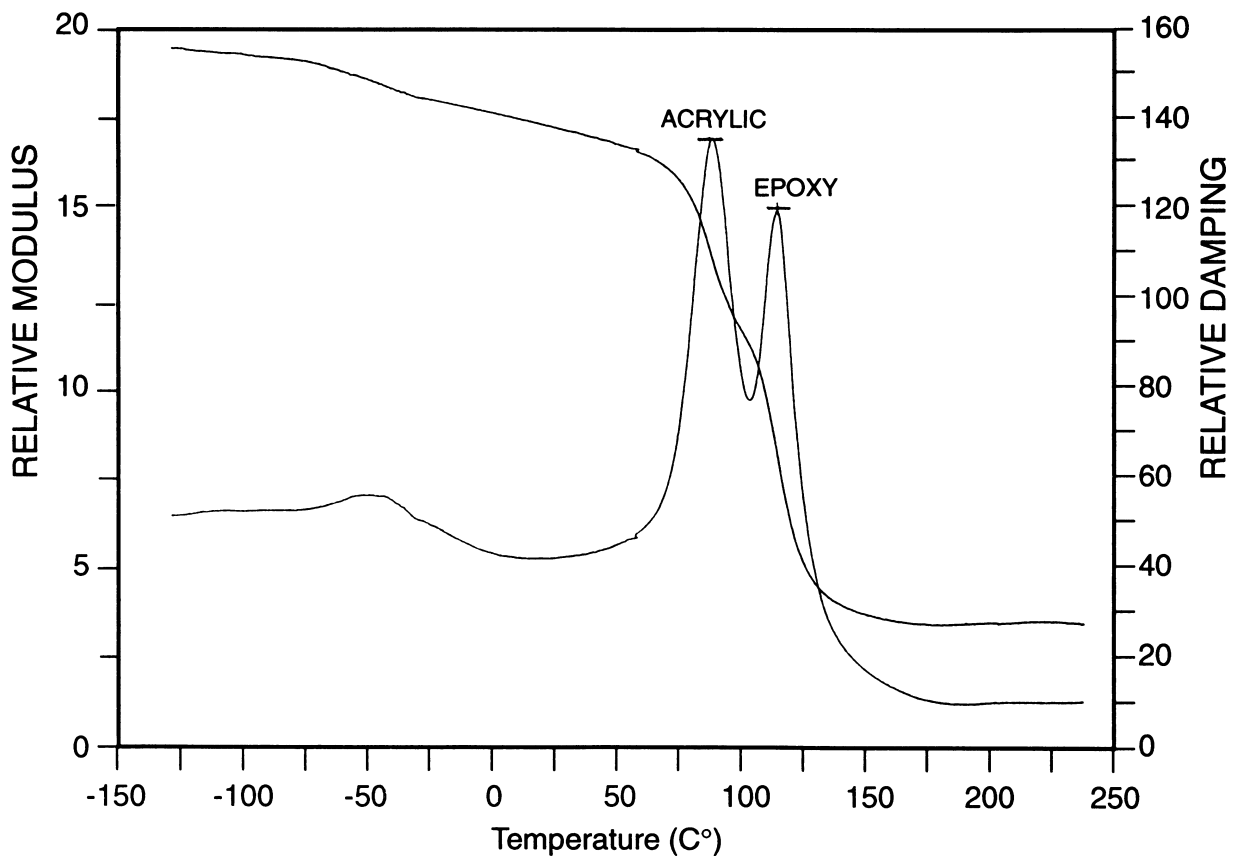
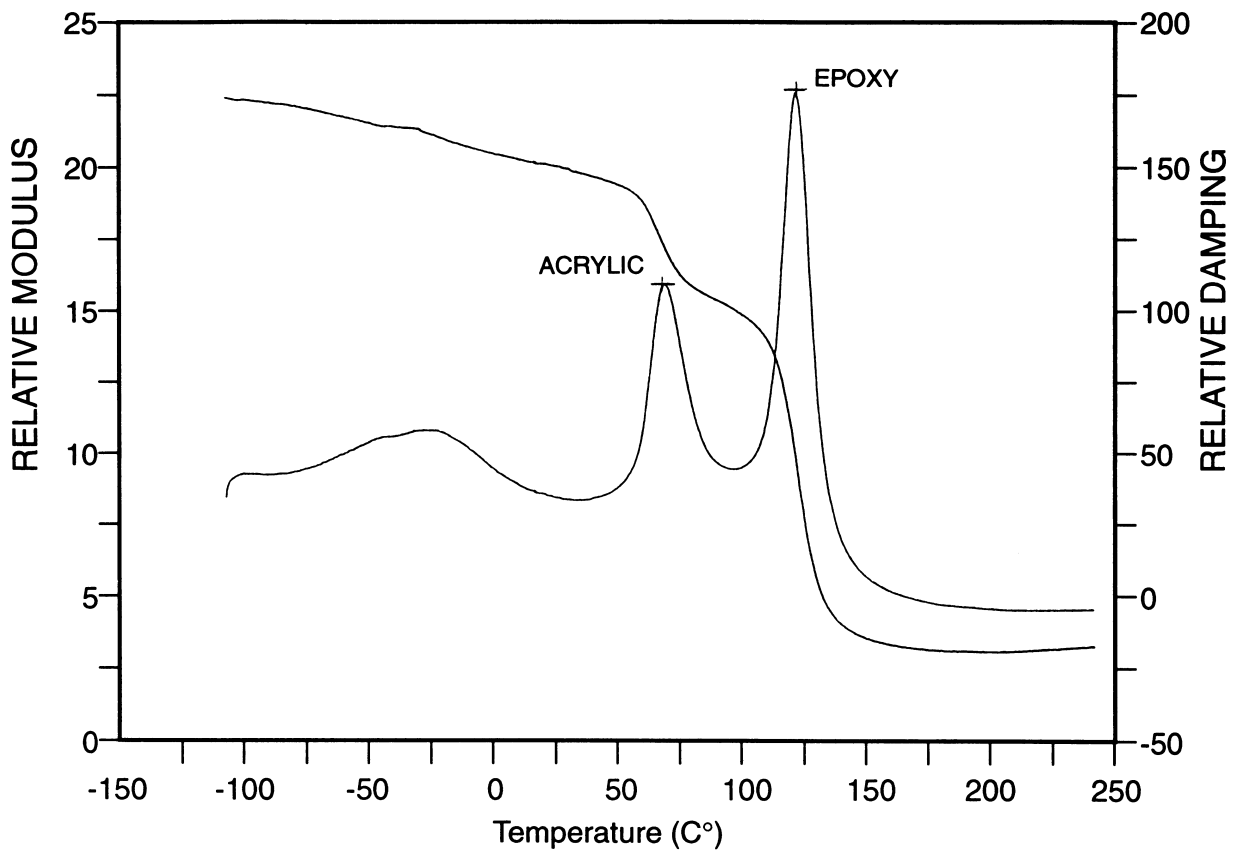


FIG. 6—Dynamic mechanical properties of epoxy/acrylic copolymers.

time allows, the best way to control thermal lag in the sample is by using step-change experiments. This kind of experiment combines slow heating rates (1 to 2°C/min) and isothermal “steps” (1 to 5 min), which allow the sample to equilibrate before heating to the next isothermal step. For thin coatings, shorter isothermal periods (1 to 2 min) are satisfactory, while thicker samples require longer (e.g., 5 min) isothermal steps.

**Strain or Oscillation Amplitude and Frequency:** In general, the greater the applied stress, the longer the relaxation time. Ideally, the sample should come close to full recovery from one applied stress before the next one begins. This means the experimenter should choose well-matched amplitudes and frequencies. For example, choosing a large mechanical deflection means that the time between the applied stresses should be longer. Conversely, higher-frequency experiments should have correspondingly smaller applied stresses. The proper relationship between the test frequency and oscillation amplitude will ensure that the sample has come close to mechanical equilibration between “events.” In most instruments, the amplitude of the deflection is based on controlled strain. In these instruments, the maximum applied strain should be at 0.1% or less. This is particularly important in filled systems (like coatings), which will exhibit nonlinear responses more readily than unfilled systems.

Because mechanical relaxation times vary widely in polymers, there are no specific rules governing the selection of oscillation amplitudes and test frequency. As a general rule, oscillation amplitudes of a few tenths of a millimeter at 1 Hz are commonly accepted practical “standards.” In very hard (brittle) or very soft materials, however, it’s generally best to perform a controlled stress (stress relaxation or creep) experiment rather than an oscillating stress experiment.

**Gas Flows:** Where possible, apply a uniform gas flow. We arbitrarily set our gas flow rates so that gas content in the oven chamber “turns over” about once every 1 to 2 min. Since the size of these chambers varies considerably, flow rates will, too. If in doubt, use the manufacturer’s recommended purge rates.

## THERMOGRAVIMETRY (TGA)

Thermogravimetry describes an analytical technique used to monitor a change in sample mass as a function of time or temperature. Depending on need, either isothermal or non-isothermal experiments are possible; nonisothermal experiments—where the sample temperature changes at a linear rate—represent the most frequently used mode. In coatings technology, the instrument is most frequently applied in compositional analysis, e.g. nonvolatile content, and for studies of thermal stability. The technique can also be applied in studies of accelerated aging, decomposition kinetics, and oxidative stability.

In recent years, improvements in commercial instrumentation have enhanced resolution to about 0.05 mg. The primary differences between the types of commercial instrumentation center on the furnace type, the quality of the software, the control of gas flow, and the sensitivity of the microbalance. In addition, high resolution TGA and a robotic system are also available. Coupled with a mass spectrometer, gas chromatograph, or FT-IR, TGA becomes a powerful ana-

lytical tool combining both physical and molecular probes in a single technique.

**Compositional Analysis**—From time to time, performance properties will change because a material supplier makes changes in the formulation or manufacture of a product. Although the supplier may not recognize it, relatively minor changes in a material can engender major changes in a coating’s performance, sometimes with a monetary consequence. Thermogravimetry provides one means for learning more about the composition of a material and when problems arise helps maintain acceptable performance. In this example, an unusual “settling” problem was traced to a subtle difference in the composition of a wax used in the paint formulation.

Other than a difference in the melt enthalpies, studies by DSC and conventional TGA (ramped at 10°C in N<sub>2</sub>) analysis revealed that these waxes were virtually identical. However, when characterized using high-resolution thermogravimetry, small but significant compositional differences between the good (A) and suspect (B) samples became apparent.

Figure 7A shows the relative weight change in these materials as they decompose to carbon-char. Weight loss follows roughly the same path, regardless of the lot tested: beginning with a small step near 175°C, weight loss proceeds through a major step at around 300°C and ends with another small step between 450 and 500°C. The derivative (%/°C) curves shown in Fig. 7B offer the best illustration of the differences between lots. Each of the peaks in this figure represents a different decomposition step or combination of steps. If these materials were truly the same, the shape of the peaks and the peak temperatures would be virtually identical, but these materials possess several differences. Most notable are those associated with the peak between 250 and 300°C: the shape and position of this peak varies significantly. Working closely with the wax manufacturer, these results helped to identify a processing error and led to narrower manufacturing specifications. Earnest [3] provides a more detailed overview of thermogravimetry and its application to compositional analysis. Table 3 describes the differences in the thermal behavior in these lots of wax.

**Volatile Organic or Moisture Content**—With ever-tightening regulatory requirements, measuring the moisture or volatile organic content (VOC) has become increasingly important in the coatings industry. Figure 8 shows the relative nonvolatile content of two polystyrene latexes. Beyond simple measurements of volatile content, the technique is an excellent way to determine the amount and rate of evolution of decomposition products.

**Thermal Stability**—TG is also used widely to monitor the stability of polymeric coatings. Figure 9 shows that the long-term degradative stability of a coating based on a vinyl-ester resin was superior to a similarly formulated coating based on an epoxy resin. The information shown here was useful in establishing the cost-effectiveness of the vinyl-ester system.

## Coatings Characterization by TGA

**Sample Preparation:** The materials typically analyzed in the coatings industry can come as either solids or liquids. Neither solids nor liquids require special preparation; they just need to fit in the pan. Like DSC, limit your sample size to

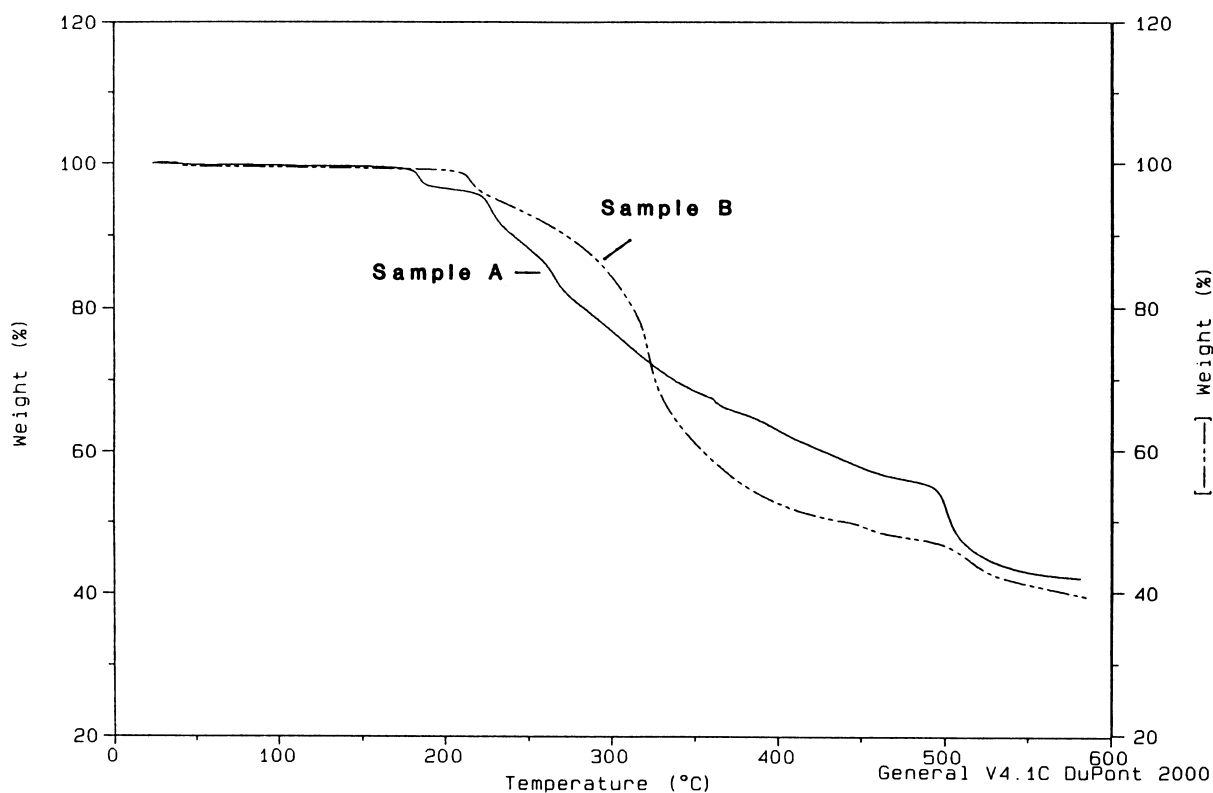


FIG. 7A—Weight loss curves for waxes with ostensibly identical compositions.

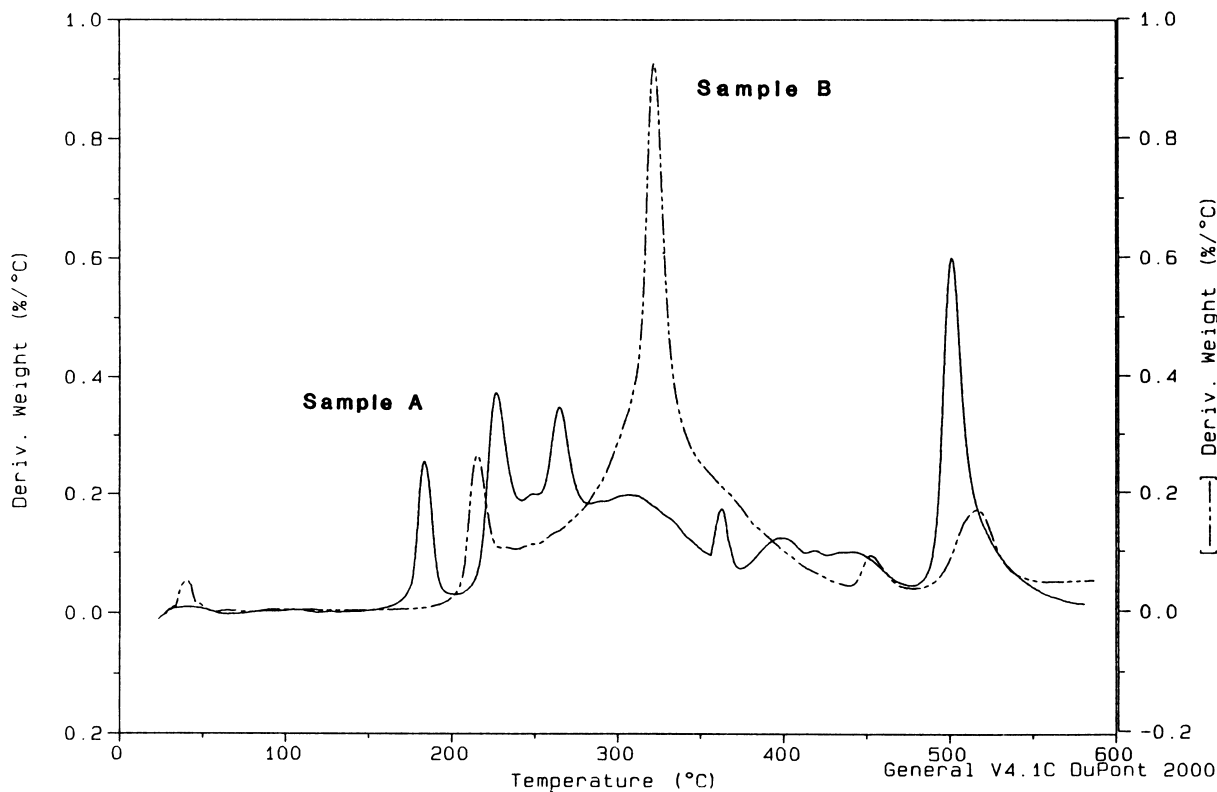


FIG. 7B—A comparison of the weight loss derivatives for the weight loss curves shown in 7A.

TABLE 3—Wax melt characteristics and decomposition characteristics.

Sample	Condition	$T_m - 1(^{\circ}\text{C})$	Total $\Delta H_m$	Decomposition Onset-1, $^{\circ}\text{C}$	% Char
A	Control, dry	87.7	75.7	172	38
B	Suspect, dry	87.4	46.1	150	43

NOTE:  $T_m$  = melt temperature.

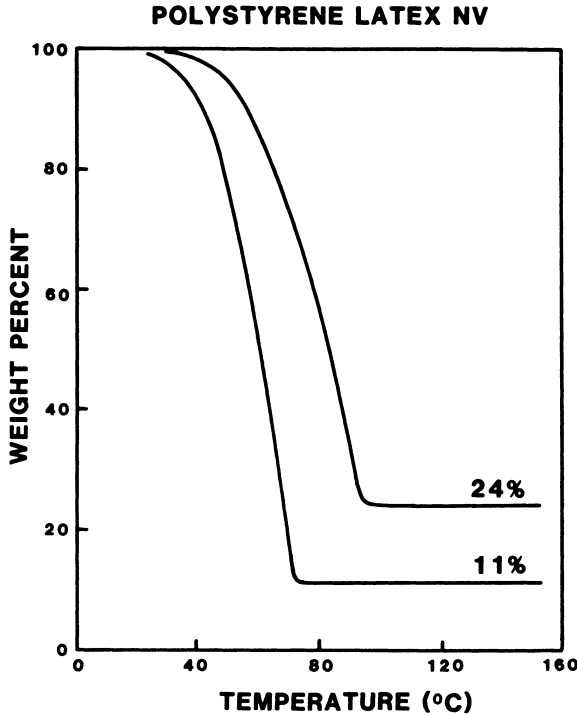


FIG. 8—Polystyrene nonvolatile (NV) content measurement obtained through TG.

somewhere between 5 and 10 mg. Large samples ( $>10$  mg) may not heat uniformly, with the outer layers heating more rapidly than the center of the sample. For solids, the physical form of the sample is very important to the resolution of the

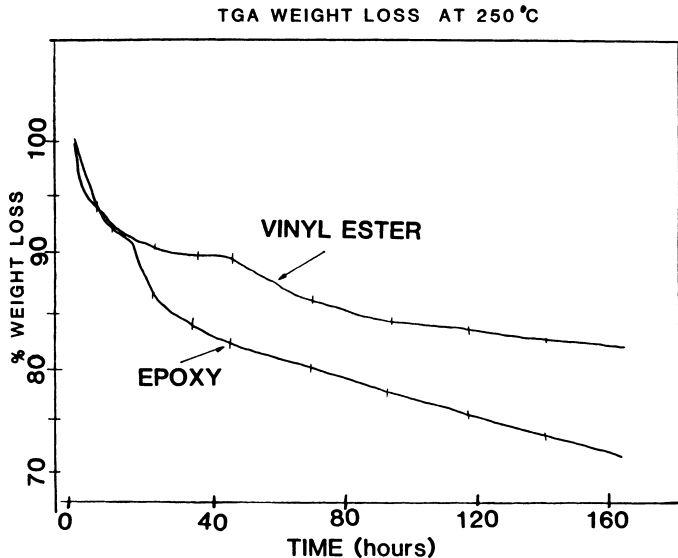


FIG. 9—Thermal stability of vinyl-ester resin.

test results. If the surface area is large, for example a powder or highly divided solid, then higher masses—as much as 40 mg—may be used without significantly reducing the sensitivity measurement. Choose the mass of a liquid sample based on the amount of solid material present, for example, use at least 10 mg of a liquid containing 50% solids. Beyond sample considerations, be aware that both aluminum and platinum—metals which are used in a typical TGA pan—can occasionally catalyze a portion of the decomposition process in some materials.

**Purge gas:** Like DSC, the selection of purge gas depends on your objectives. High-purity dry nitrogen (99.99%) is typically used. It offers the benefit of low cost and reasonably good heat transfer. Argon, another frequently used gas, improves heat transfer and may improve the resolution of the analysis but only at increased cost. In some instances, you may want to control the humidity of your purge gas. A simple, low-cost method involves bubbling the purge gas through DI water in a bubble tube and running the effluent into the instrument. Relative humidity values can reach 80% using this approach. Purge rate requirements vary with the instrument.

**Temperature Range and Heating Rate ( $\beta$ ):** In most compositional analyses, our experiments are run between room temperature and  $600^{\circ}\text{C}$ . This temperature range suits most coating systems because, as a rule, polymers (coating binders) usually begin to decompose somewhere between  $250$  or  $350^{\circ}\text{C}$  and are gone by  $450^{\circ}\text{C}$ . When running liquids, pay very close attention to the instrument's set-up time before it begins to collect data. In highly volatile materials, as much as 10% of the volatile material can be lost before the first data point is collected in the experiment. The difficulties with interpretation in this situation should be obvious.

The most important consideration in selecting a heating rate for your experiments is heat transfer and the steady-state condition of the sample. For routine analysis, a  $10^{\circ}\text{C}/\text{min}$  nonisothermal temperature ramp offers a good compromise between run time and resolution. Keep in mind that high heating rates can produce thermal lag within the sample, which in turn will broaden transition regions. In instances where a sample exhibits two or more weight loss transitions, they will tend to run together at higher heating rates. Slower heating rates are usually used where there is a need for improved resolution and run time is not a concern. Where isothermal temperatures are necessary, choose an experimental temperature most representative of the end use requirements.

A few instrument vendors offer "high or enhanced resolution" capabilities, a technique which, in essence, combines the virtues of a rising temperature experiment with the benefits of an isothermal experiment. Whatever the manufacturer's recommendation, make certain that the gas flow rates are identical for each part of your experiment. Analyzing the same sample with even small variations in gas flow (less than  $5\text{ mL}/\text{min}$ ) can produce dramatic changes in the weight loss curves or the weight loss derivative curves. In fact, one mate-

rial can appear to be two simply because of differences in the purge gas flow rate. These differences occur because the degradation mechanism is sensitive to temperature and holding the sample under near isothermal conditions can amplify a mechanistic step that would normally play a minor role in a standard rising temperature experiment. All of these precautions serve to emphasize one important fact: the experimenter must have a good grasp of the chemistry of decomposition when performing these experiments. Otherwise, he runs the risk of misinterpreting the results obtained for the decomposition process.

**Data Collection:** Try to average between two and eight data points per degree Celsius increase, depending on the experimental objectives. Higher heating rates require higher data collection rates in order to obtain the resolution obtained at lower heating rates. In some commercial instrumentation, the data collection rate can be varied from low to high at various steps in the experimental procedure. Note that high data collection rates at slow heating rates can produce large data files (using valuable disk space!) while yielding little or no improvement in the resolution of the data.

## THERMOMECHANICAL ANALYSIS (TMA)

Thermomechanical experiments measure changes related to sample dimension as a function of time or temperature. These changes depend on both viscous (energy dissipative) processes and elastic (energy storing) processes within the material. Daniels [35] linked thermally dependent changes in dimension with various kinds of molecular motion: changes in dimension correlate with chemical reactions, lattice vibrations, changes of state, the glass-rubber transitions, changes in crystalline structure, or some combination of these phenomena. Riga and Neag [36] and Earnest [37] provide a thorough review of thermomechanical techniques and application in materials science.

The techniques associated with TMA are broadly applicable in materials science and are used in characterizing liquids, polymers, and inorganic materials. In practice, TMA is most commonly used in assigning transition temperatures or determining the coefficient of linear thermal expansion ( $\alpha$ ) by linear dilatometry. Descriptions of thermomechanical analysis (TMA) generally include linear dilatometric techniques because the same instrument can be used for thermomechanical and thermodilatometric experiments. When changes in sample dimensions are measured with a negligible load, the technique is more properly referred to as linear thermodilatometry (TDA). Depending on the experimental objective, any one of several probe types may be used.

TDA is typically applied in studies of ceramics, glasses, and metals—materials that exhibit a primarily elastic response (particularly for  $\alpha$ )—or for determining glass transition temperatures ( $T_g$ ) in polymeric materials. Dilatometric experiments are usually applied over a range of temperatures repre-

sentative of the product's end use, but may begin near absolute zero and reach as high as 2500°C [35]. Thermomechanical analysis is most often applied in characterizing polymers or composites (e.g., most coatings), where the viscoelastic properties of a substance often dominate the material response. Thermomechanical studies usually employ a narrow range of experimental temperatures, typically falling between -175 and 850°C.

**Instrumentation**—The kind and quality of information obtained from a thermomechanical analyzer depends primarily on the arrangement of the sample and probe type. The penetration mode is probably the most commonly used arrangement in TMA and is usually used in assigning transition temperatures, such as the glass transition temperature or softening point temperature, in polymeric materials. In this mode of operation, substrate effects become increasingly important as the sample thickness decreases. This is particularly true in the analysis of thin films and coatings [38]. Tension tests are often used in characterizing the properties of thin films. In fact, improvements in instrumentation, particularly in controlling the applied force and fully automated operation, make possible the characterization of more fundamental viscoelastic properties such as creep and stress relaxation. These improvements have also increased the resolution of these instruments considerably. The resolution of these instruments ranges from about 500 nm in first-generation commercial instruments (ca. 1975–80 and earlier) to claims of less than 5 nm in second-generation instruments.

**Dilatometry**—This method has broad applicability in coatings technology, such as in determining the coefficient of thermal expansion (CTE). It is particularly valuable in failure analysis. For example, mismatches in CTE appear to play a role in the failure of two-coat systems such as gel coats.

Gel coats are polyester/styrene systems that are sprayed directly onto a mold surface and allowed to advance to a tack-free state. A fiberglass mat is then placed onto the partially cured gel coat and a reinforcing laminating polyester resin applied to the fiberglass mat. The laminate is removed from the mold after reaching optimum cure under ambient conditions. If the gel coat or laminating resin is improperly formulated or undercured, differences between the CTE values may be large enough to cause delamination at the interface.

Ideally, the CTE values for the members of the part should be the same or only slightly different. In this instance, however, the differences in CTE values shown in Table 4 led to delamination and the eventual failure of the part. Subsequent analysis of residual heat of reaction by DSC showed that the gel coat was improperly cured. Inadequate cure led to appreciable differences between the CTE values of the gel coat and laminate, and ultimately, to the failure of the system. Figure 10 provides a comparison of the CTE curves for the gel coat and polyester laminating resin.

TABLE 4—Gel coat and laminating resin CTE values (PPM/°C).

Material	No. of Runs	Avg CTE	Standard Deviation	Range
Gel Coat	4	5.0	0.2	5.0–5.3
Laminating Resin	5	5.9	0.1	5.8–6.1

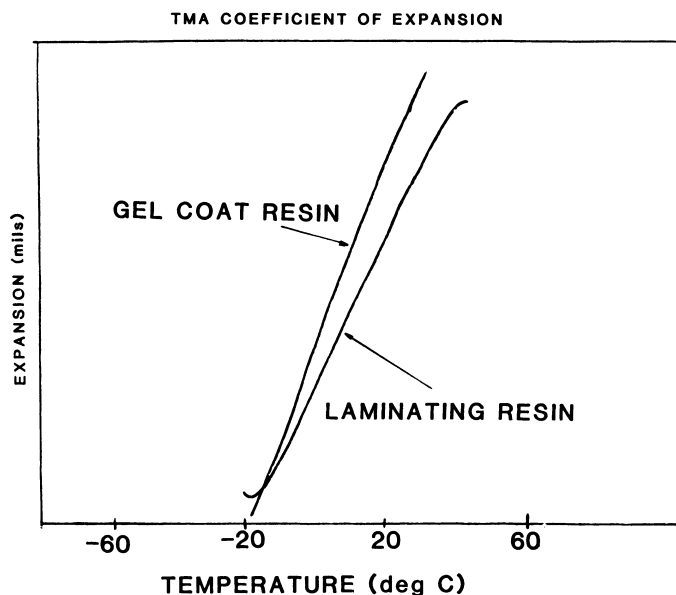


FIG. 10—A comparison of the CTE curves for the gel coat and polyester laminating resin.

### Thermomechanical Analysis

Softening point temperatures (SPT) and total probe displacement obtained using thermal mechanical analysis provide valuable insight into a coating's performance, particularly in comparing the relative degrees of cure in production materials. For example, when cure levels in two container coatings were compared—one of which failed QC tests after manufacture—TMA results strongly suggested that the failed coating was undercured. The TMA results in Table 5 show that the failed coating had a lower softening point temperature and greater total displacement than the coating that passed. Rebaking the failed coating led to an increase in SPT and a decrease in probe penetration. While the changes in SPT and probe displacement indicate an improvement in performance, they still failed to match those of the coating that passes the QC test. Intentionally undercured coatings yielded similar results, strongly suggesting that the coatings that passed reached a higher degree of cure than the coating that failed. Perhaps more importantly, these materials were characterized directly on the container substrate, indicating the TMA's value in situations not amenable to characterization using more routine analytical methods.

### Coatings Characterization by TMA

**Sample Preparation:** Sample preparation requirements vary depending on the test mode, usually either force/deflection (penetration) or dilatometric experiments. Either free films or coated substrates can give excellent results.

While free films are probably best—provided that they lay flat and retain their shape during the experiment—it's usually more practical to run TMA experiments with coated substrates. If you use a coated substrate, pay close attention to sample thickness, the dimensional stability of the substrate during the experiment, and the size of the sample in relation to the probe tip. The larger the sample in relation to the probe tip, the better.

Substrates, like the coating, can change with experimental conditions and consequently influence experimental results that an experimenter might attribute to coating properties alone. The best way to avoid substrate effects is to increase the thickness of the sample. Ideally, samples should be about 500  $\mu\text{m}$  (20 mils) thick, but films this thick are rarely found in any application. Moreover, increasing the thickness of the sample may improve resolution at the expense of validity. In practice, films measuring 20  $\mu\text{m}$  (about 1 mil) will yield excellent quantitative results. In general, if you can make the sample thicker without compromising the validity of the results, you should. The need for thick samples doesn't mean that thin samples may not be tested. In fact, significant *qualitative* results can be obtained at film thicknesses as small as 5  $\mu\text{m}$  provided that the sample preparation conditions are extremely well controlled.

If you have doubts about potential substrate effects, analyze the uncoated substrate and try to determine if the substrate will contribute to changes in the TMA's response. Some software packages will allow you to subtract baseline effects from the total response of the coated substrate. As with the DMA, ensure uniform thermal histories by preparing specimens in a controlled environment.

**Heating Rate:** For most applications, use heating rates around 5°C. The primary consideration in selecting a heating rate are potential problems with thermal lag in the sample. Temperature gradients within the sample can broaden transition regions and force them to occur at artificially high temperatures. In contrast, slow heating rates allow the entire sample to equilibrate to temperature change, which, in turn, improves the accuracy of transition temperature assignments.

**Applied Force:** This only applies to penetration experiments because dilatometric experiments require that the probe be brought into very light contact with the sample. In penetration experiments, applying very low forces may not provide adequate change in the sample to accurately monitor subtle transitions during an experiment; conversely, large forces may actually damage the sample during an experiment. In instruments that use weights, the applied force should be between 5 and 20 g. In servomotor-controlled TMAs, use 0.05 to 0.2 N forces for probe tips with a 0.4-mm radius.

**Gas Flows:** As with all of the instruments, purge gases provide a stable test environment and ensure uniform heat transfer to the sample. Use the manufacturer's recommended purge rates for all experiments.

TABLE 5—TMA softening point temperatures (°C) and probe displacement values ( $\mu\text{m}$ ).

Material	Production SPT	Probe Displacement	Rebake SPT	Probe Displacement
Passed	100	1.1	104	0.3
Failed	91	4.8	99	0.9

**Special Applications:** Many of the newest commercial TMA's are quite versatile instruments and come with special attachments for performing unique experiments. For example, most TMAs come with clamps for tensile testing—good for measuring everything from tensile modulus to shrinkage with age or cure. These techniques almost always require special preparation and operating conditions. Work closely with the supplier when designing these experiments, or, better still, ask the manufacturer for a contact familiar with the technique.

## DIELECTRIC ANALYSIS

Dielectric thermal analysis (DEA) is a convenient nondestructive test that relates fundamental molecular motions to a variety of polymeric properties. Applications in coatings science include the characterization of new materials and processes, cure studies, film formation studies, formulations optimization, applications development, performance prediction, competitive product evaluation, and QC/QA applications. General descriptions of dielectric properties can be found in a variety of papers [27,39–41].

Because engineering limitations prohibit the characterization of the complete continuum of dielectric properties, there are a number of commercial dielectric analyzers available, each offering advantages in their potential range of applications. The operating principle of all of these instruments, however, is the same: a polymeric system is polarized in an electrical field and the time, temperature, and frequency-dependent dielectric relaxations monitored. Commercially available instruments may be divided into two broad categories: those polarizing samples with an alternating current (ac) and those using a direct current (dc). Each instrument may also have one or more sensors or analytical configurations; these include remote single-surface, ceramic-single-surface or parallel plate geometries.

All dielectric analyzers measure two fundamental electrical characteristics of a material—capacitance and conductance. Capacitance measures a material's ability to store electrical charge, and conductivity measures its ability to transfer electric charge. These components are used to determine geometry-independent values for the material's permittivity ( $\epsilon'$ ) and loss factor ( $\epsilon''$ ), serving as molecular probes that correlate with the changing chemical and physical states of the material. Permittivity corresponds to the alignment of dipoles in the electrical field; permittivity values are relatively low at temperatures below  $T_g$  or in highly cross-linked polymers and relatively high above the  $T_g$ . The loss factor corresponds to the amount of energy required to align dipoles and move ions in the electrical field. The latter term is frequently used in monitoring rheological changes during processing or for monitoring the progress of a cure reaction. More complete descriptions of the use of dielectric analysis in thermal analysis [9], film formation [42], and thermoset cross-linking [43–45] can be found elsewhere.

Thermally stimulated current (TSC) represents a relatively new approach where dipole moments are polarized in a d-c field at temperatures above the sample's main transition temperatures [46]. Following polarization, the sample is quenched to a low temperature, and then scanned at a constant heating rate through the polarization temperature. As the

sample depolarizes, the charge stored in the polarization process is then measured as a function of time. Current peaks obtained this way correlate well with transition temperatures obtained by mechanical relaxation, DSC, or by a-c dielectric spectroscopy.

Another d-c technique—relaxation map analysis (RMA)—is closely allied to TSC and represents a sophisticated extension of TSC experiments. According to theory, this procedure isolates the individual relaxation modes that constitute a typical TSC by varying the polarization temperature and monitoring the depolarization current over small (less than 5°C) temperature “windows.” In this way, individual relaxation modes can be isolated from the entire spectrum of modes that make up a typical TSC curve. An Arrhenius plot of the individual relaxation times forms a relaxation map for a material. Coatings characterization using TSC and RMA is described in more detail elsewhere [47,48].

Although the dielectric techniques date back to the early 1900s, the lack of high-quality equipment and the attendant experimental difficulties limited the value of DEA for coatings characterization and in materials science generally. Advances in engineering design have dramatically improved the utility of commercial DEAs and rekindled interest in the technique. DEA now promises to play an important role in coatings characterization. The two examples described here—powder coating cure and resin characterization—underscore the value of DEA for coatings characterization. Ceramic single-surface sensors were used in both of the studies.

**Powder Coatings**—Changes in the complex permittivity  $\epsilon^*$  of unpigmented powder coatings were correlated with the melt transition (about 60°C) and the onset of cross-linking (about 100°C) in these powders. Dielectric measurements, particularly transition temperatures and relative intensities, correlated very well with DSC results. Five powders, each formulated at different cross-linker levels, were scanned during and after cure. Figure 11 illustrates a typical DEA plot combined with results from the DSC. As the results show, major transitional features in these two sets of data correspond closely. One significant deviation occurs in the region between roughly 65 and 80°C where  $\epsilon^*$  exhibits a dramatic increase at all frequencies; there is virtually no DSC response over the same temperature range. The increase in  $\epsilon^*$  probably coincides with increasing molecular mobility as the polymer's volume increases above the melt. Dielectric properties should change rapidly over this temperature range while changes in enthalpy (and therefore DSC heat flow measurements) should be minimal.

**Resin Properties**—A comparison of the dielectric properties of an appliance powder coating formulated with polyester from two different manufacturers reveals distinct differences. Figure 12 reveals differences in the breadth of the melt transition and the cure onset temperature. Although the performance properties of the resins were indistinguishable, the DEA results clearly indicate the technique's sensitivity to relatively small differences in materials that were virtually identical by all other measures.

**Film Formation**—The complexity of the film formation process in coatings, particularly latex coalescence, makes this

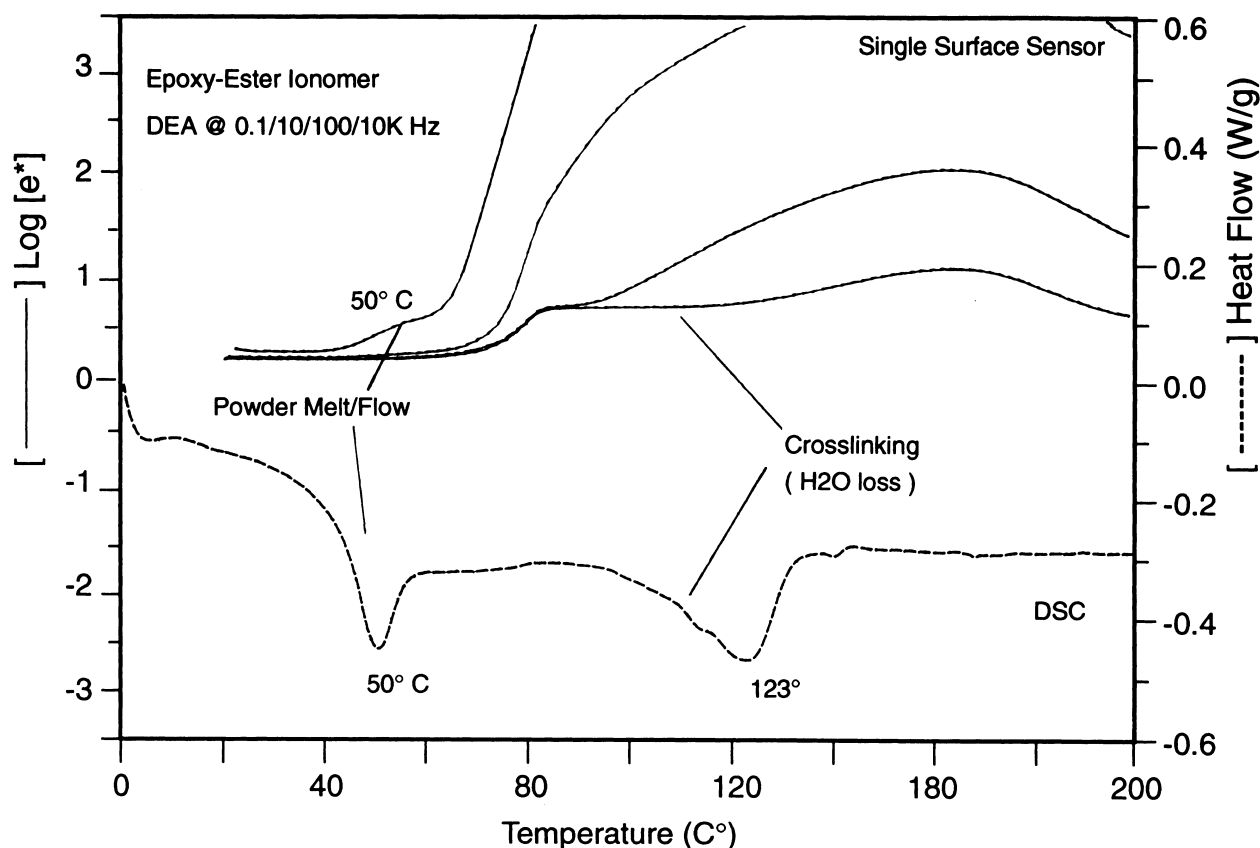


FIG. 11—DEA and DSC results for powder coating cure.

a difficult subject to characterize and understand. Improvements found in newly available dielectric analyzers indicate that DEA will offer, at the very least, a significant step forward in our ability to follow film formation. Figure 13 follows the change in the dielectric constant (complex permittivity) in two latexes, one catalyzed and the other uncatalyzed, after they were applied to a DEA sensor. By comparing the changes in  $\log e^*$  with the observations from optical microscopy, DSC and TGA (results not included here), some inferences about the nature of the film formation process were made. In the catalyzed sample, the drop in  $e^*$  over the first 20 min of the experiment correlates to the loss of free water. Between roughly 20 and 30 min, the latex particles begin to deform and pack tightly together. Finally, over the next hour or so, there is a loss of ionic mobility that probably coincides with polymer interdiffusion at the particle-particle interface. The catalyzed latex had formed a clear, uniform film by the end of the experiment.

The dielectric behavior of the uncatalyzed film was far different. While changes in permittivity associated with water loss and particle packing were evident, the lengthy period thought to correlate with interdiffusion was missing. In fact, this latex was a poor film former, leaving an opaque, severely cracked film on the surface of the sensor.

### Coatings Characterization by DEA

**Sample Preparation:** This depends very much on the type of sensor used. Parallel plate sensors are typically used for

free films, while film formation studies would typically employ single-surface sensors. As with other approaches, free films should be made in well-controlled environments and *must* meet the minimum film thickness specifications of the manufacturer. Whenever possible, though, the sample thickness should closely approximate the thickness of the coating after application. As noted earlier, free films can be made by coating low-energy surfaces like PTFE or polypropylene or coating thin aluminum sheet stock and dissolving the aluminum (after the film has formed, of course) with an alkali.

Single surface sensors can be used for any material, but they are especially useful for studying liquids or materials that require a gas/polymer interface for proper analysis. Applying liquids, for example in film formation studies, often requires special preparation to ensure that the electrode surface is completely and evenly covered. For example, when studying low-viscosity liquids, we first calibrate the sensor, then build a low silicone polymer border at the edge of the electrode to keep the sample in place. The volume of liquid applied should leave a final film roughly twice as thick as the distance between electrodes when the sensor uses interdigitated comb electrodes. Always use analytical pipettes to ensure that the applied volume is uniform from experiment to experiment. While absolute measurements of dielectric properties may be in doubt using this approach, it is a valid way to make relative comparisons provided that each material is prepared and handled in *exactly* the same way.

**Frequency Selection:** In general, there are two components of the dielectric response to an applied electrical field: dipole polarization and free charge migration. The former is most frequently associated with high frequencies (100 kHz or



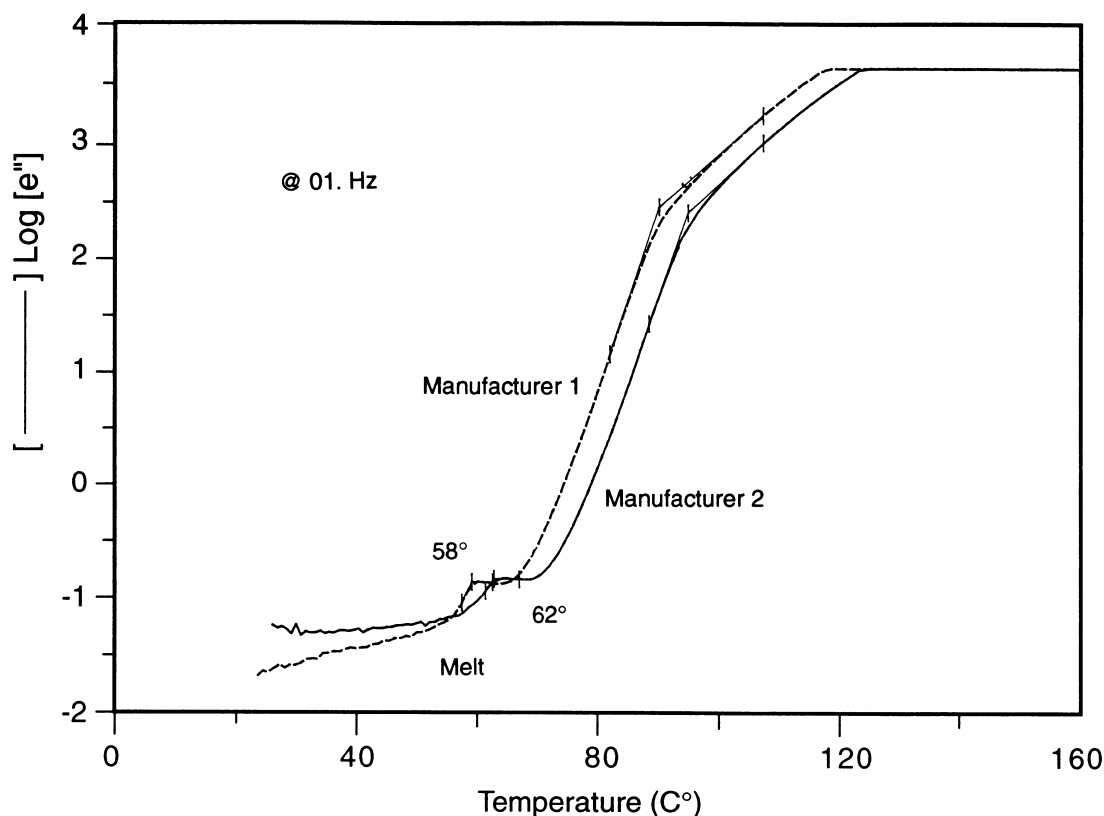


FIG. 12—A comparison of the dielectric properties in identically formulated resins from two manufacturers.

more) while the latter is associated with lower frequencies. Because the dielectric response of polymers varies widely in polymers (and sometimes within classes of polymers), there are no specific rules governing the selection of a test frequency. As a general rule, apply as broad a range of frequencies as your equipment will allow early in the experimental process. After the kinds of responses for given material are better understood, use more limited frequency ranges in subsequent experiments.

**Heating Rate:** This is an extremely important factor that depends inherently on the frequencies selected for an experiment. Our heating rates are chosen to ensure that we have approximately one data point for each °C increment at each frequency. Low frequencies (<0.1 Hz) require slow heating rates so that the sample has reequilibrated after imposing the a-c electrical field. For example, if we choose to test at frequencies ranging from 0.1 Hz to 100 kHz in order of magnitude increments in our equipment, then a complete cycle (six frequencies) takes about 1.1 min. Based on this cycle time, we would choose a 1°C/min heating rate. Cycle times are much faster at higher frequencies, usually less than 0.2 min, so correspondingly higher heating rates may be used. In isothermal studies we usually collect about 6 to 12 data points per applied frequency for each minute of the experiment depending on the length of the experiment.

**Gas Flows:** Where possible, apply a uniform gas flow. As with the DMA, we set our gas flow rates so that the oven chamber “turns over” about once every 1 to 2 min. Since the size of the oven chambers in various instruments varies con-

siderably, flow rate requirements will as well. If in doubt, use the manufacturer’s recommended purge rates.

Most DEAs are also excellent instruments for running controlled atmosphere experiments. For example, controlled humidity experiments (to 80% RH) require bubbling the purge gas through water (or a salt solution of known humidity) before entering the instrument chamber.

## THERMOSET CURE STUDIES

The interrelationship between the network formation process and performance properties make cure process studies critically important in product development. A thermoset coating’s performance properties depend inherently on cure conditions. Important characteristics of the cross-linking reaction include the gel point,  $T_g$ , and the kinetics of the cross-linking reaction. These properties establish a quantifiable link between the cure reaction and the development of thermoset properties. In essence, they provide a way to “picture” the cure process and a tool for optimizing materials handling, processing, and cure.

Characterizing cure behavior also helps to distinguish between complete cure and optimum cure, an important distinction in thermoset applications. Completely cured thermosets are “ideal systems” where the cross-linking reaction has reached 100% conversion and properties are constant for practical purposes. Optimally cured thermosets are “non-ideal” systems where the cross-linking reaction is incomplete and satisfactory performance properties rather than 100%

Sample: RCR0327 Si Chemistry  
 Size: 2.500 mm  
 Method: Si DEA  
 Comment: Catalyzed vs Uncatalyzed Si-latex System

DEA

File: C: SIDEA.03  
 Operator: Neag  
 Run Date: 2-Feb-90 10: 06

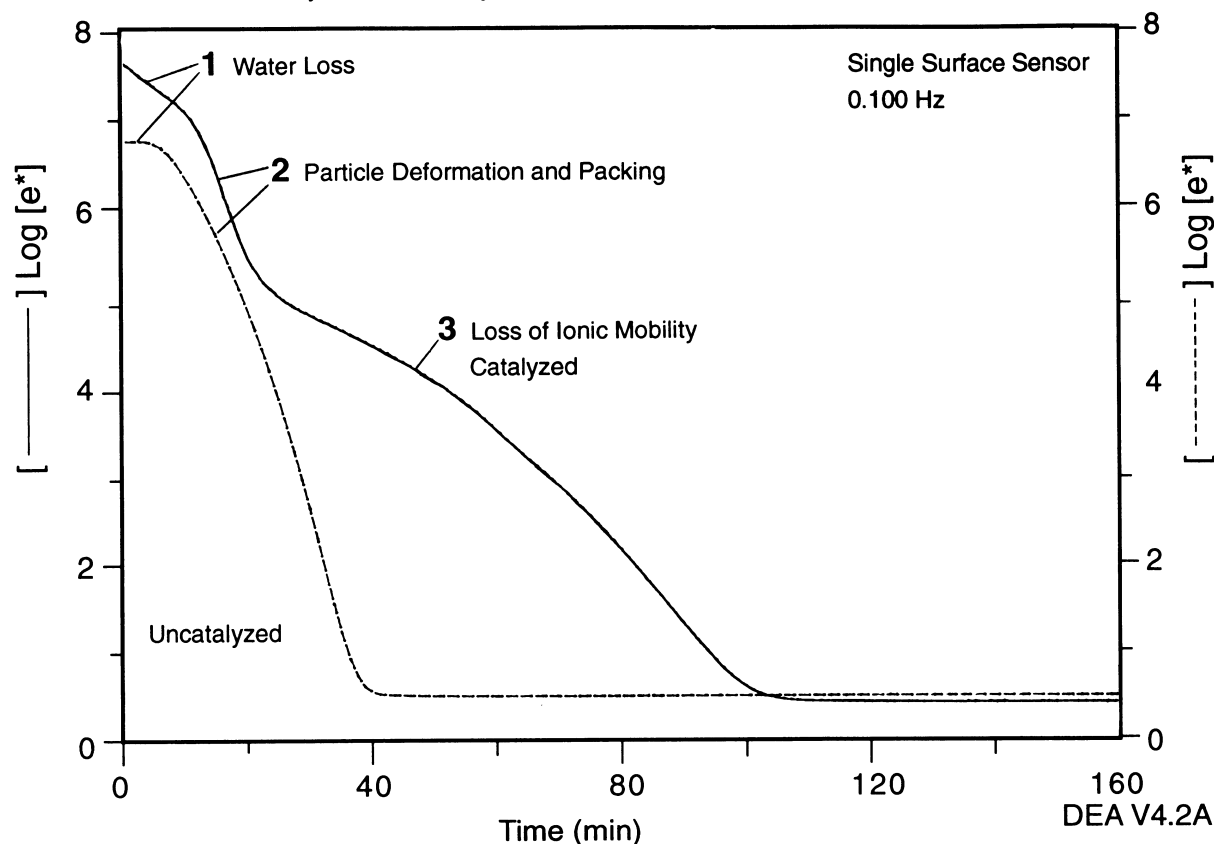


FIG. 13—Changes in complex permittivity during latex film formation.

chemical conversion mark the end of the cure process. In practice, coatings can usually be categorized as nonideal thermosets.

**DSC Cure Studies**—DSC cure studies have been particularly beneficial in optimizing cure schedules for gel coats—polyester/styrene thermoset coatings used in marine and sanitary applications. The initiation of the cure reaction in gel coats begins with the decomposition of a peroxide and the subsequent copolymerization of styrene with unsaturated groups in the polyester resin backbone [49]. When fully cured, these systems are highly cross-linked. Elementary kinetics analysis [50] indicates that the reaction order should be 1.5, first order in monomer and half order in initiator.

Evaluation of the kinetics of the gel coat cross-linking reaction using DSC and FT-IR agreed remarkably well. The data in Table 6 also show that the order of reaction obtained by both DSC and FT-IR almost match the value of 1.5 obtained using a theoretical kinetics approach.

TABLE 6—Kinetics parameters for the cure of gel coat resins.

	$n$	$E$ , kJ/mole	$\ln A$ , $s^{-1}$
DSC	1.56	105.0	28.4
FT-IR	1.54	107.6	29.2

DSC studies revealed that the onset of the gel coat cure process corresponds to the decomposition of the peroxide initiator; according to these results, the reaction began at about 75°C and ended just prior to 150°C. The temperature range (72 to 148°C) selected for the kinetics evaluation using DSC was based on FT-IR spectra. These results showed that the reaction of styrene, and presumably its reaction with the polyester, began and ended at similar temperatures in the DSC and FT-IR. FT-IR reaction kinetics were based on the disappearance of the styrene vinyl group ( $779\text{ cm}^{-1}$ ). While both methods produced excellent results, the DSC results were obtained in a single temperature sweep, while the FT-IR results required significantly more experimental effort to produce and analyze. Results for gel coat cure by DSC, FT-IR, and also DMA are covered in detail elsewhere [51,52].

**DMA Cure Studies**—As a thermoset cures and the number of cross-links increases, a coating's modulus, or resistance to deformation, also increases. In dynamic mechanical analysis, a rise in resonant frequency or relative modulus parallels the development of properties during network formation. The characteristic rise in relative modulus—particularly its rate and intensity—reveals much about the cross-linking process. The curves in Fig. 14 illustrate how a coating's relative modulus (or stiffness) and damping (energy dissipation) change during cross-linking or film coalescence. Throughout the

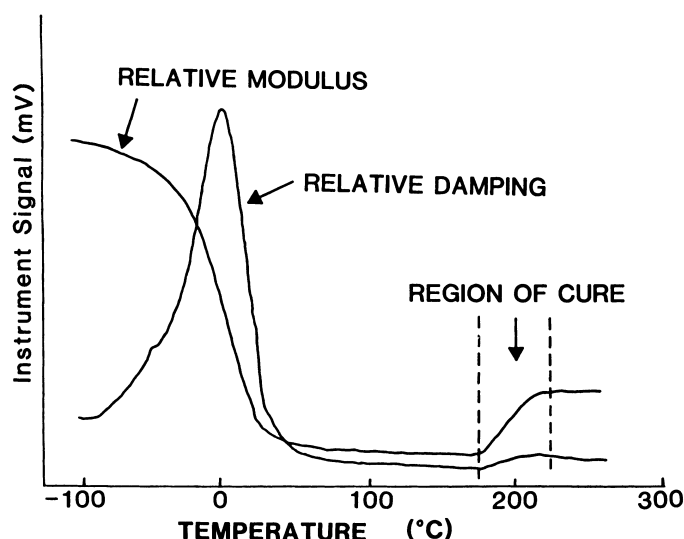


FIG. 14—Generalized dynamic mechanical cure response.

glass transition region—between roughly  $-80$  and  $20^{\circ}\text{C}$ —the relative modulus of the sample decreases until it reaches a minimum. Between  $50$  and  $180^{\circ}\text{C}$ , the coating is really a low-viscosity liquid that has little measureable dynamic mechanical response. The only measurable mechanical response in this region is due to the substrate used in the experiment. As the temperature increases, cross-linking (or film coalescence) begins and the relative modulus begins to rise. When the reaction is complete, about  $220^{\circ}\text{C}$  in this example, the development of mechanical properties reaches a plateau.

Cure studies by DMA can also help explain the interrelationship between cross-linker characteristics and the cure process. Figure 15 shows the change in the rate and degree of cure in relation to the reactive groups on melamine cross-linkers. As the imino ( $-\text{NH}$ ) concentration increases, the rate and degree of cure both increase. At low imino levels, the rate and degree of cure are low; beyond about  $15\%$   $-\text{NH}$ , the rate of cure changes significantly, while the DOC appears to reach an asymptotic limit.

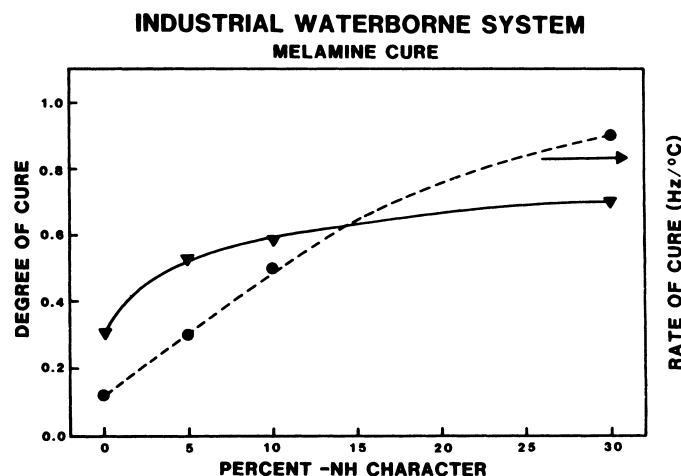


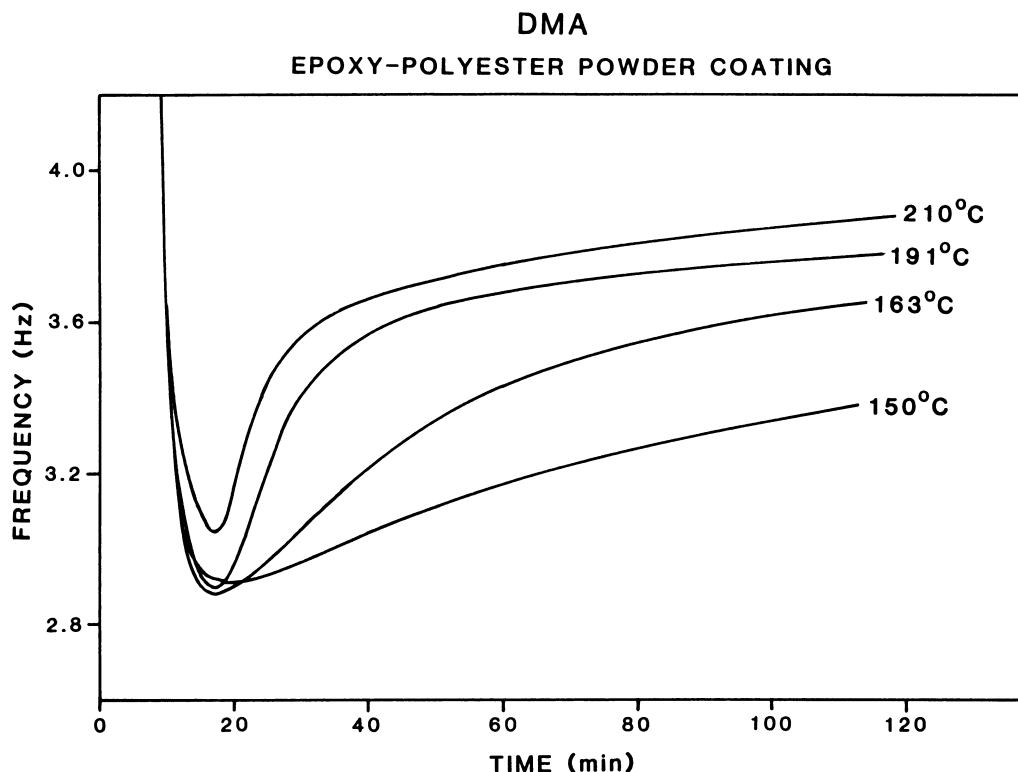
FIG. 15—The relationship effects of cross-linker characteristics on the rate and degree of cure of a waterborne coating.

When the experimental objective is to make a quick comparison of the effects of formulation variables like cross-linker levels or catalyst levels, simple cure curves like these offer an excellent way to make qualitative judgments about the cure process. Sometimes, however, customers may demand more than simple “faster/slower” or “more/less” comparisons. For example, a customer may want to know how long the film formation process will take under a variety of cure conditions different, often substantially different, from those used in past experiments. In cases like these, models of the film formation process are a valuable tool for predicting the time required to complete the film formation process. The virtue of modeling lies in its ability to provide a well of information from a relatively small database or, in this case, a few film formation experiments.

The time-temperature superposition (TTS) approach, while somewhat more demanding experimentally, is a far more versatile method for characterizing the cure process than individual cure scans. This approach uses a series of isothermal cure curves (usually four) to determine the activation energy for the cross-linking process. Once the activation energy is known, an Arrhenius model is used to predict relative rates of cure at different isothermal cure temperatures. The curves shown in Fig. 16 illustrate portions of the storage modulus curves typically used in TTS cure studies. These curves were obtained for an epoxy-polyester powder cured at four isothermal temperatures. The characteristic form of these “cure” curves discloses several important aspects of the cross-linking process, such as the time to gelation, the rapid increase in relative modulus during cure, and a plateau region that marks the end of the cross-linking process.

From a processing perspective, the onset of the rise in modulus about 3 min into the “bake” scan represents the most important feature of the curve. The onset of the rise in frequency in these curves approximates the time to gelation, or the point where the polymer transforms from a viscous liquid to an elastic gel; this point marks the processing limit of the thermoset. Beyond this point, cross-link density increases, approaching a plateau which marks the end of the cross-linking process. In Fig. 16, these powder coatings fail to reach this plateau, even at the highest cure temperatures and/or longest cure times. The continued rise in relative modulus indicates incomplete network formation, even after 100 min at temperatures as high as  $210^{\circ}\text{C}$ . Longer cure times or higher cure temperatures would eventually establish the endpoint of the cure process. The modest increase in relative modulus at later cure times may be related to annealing effects or some combination of cure and annealing. Generally, thermosets cured to the plateau will possess less damping, have higher  $T_g$ 's, and are more brittle than thermosets cured to a point below the plateau.

Degree of cure curves for powder coatings were obtained from DMA data by measuring the increase in relative modulus (measured as a frequency increase here) occurring as cross-linking proceeds. The DMA degree of cure was calculated from Eq 1 below. This equation allows the estimation of the relative degree of cure between the gel point (0% DMA DOC) and the fully cured thermoset (100% DMA DOC). In these experiments, the gel point is defined by the initial rise in the modulus curves. This point in the modulus curve marks the formation of an intractable gel. Full cure is defined by the



**FIG. 16—Dynamic mechanical cure response of an epoxy polyester powder coating at four isothermal temperatures.**

plateau region of the modulus curve occurring just after the sharp rise in modulus.

DMA DOC is defined as:

$$\text{DMA DOC} = \frac{\text{Hz}(t, T) - \text{Hz}_{\min}}{\text{Hz}(\infty, T) - \text{Hz}_{\min}} \quad (1)$$

where  $\text{Hz}(t, T)$  is the frequency measured during cure at time  $t$  and isothermal temperature  $T$ ;  $\text{Hz}_{\min}$  is the minimum pregelation frequency (roughly equivalent to the resonant frequency of uncoated stainless steel mesh) and  $\text{Hz}(\infty, T)$  is the frequency of a fully cured coating at temperature  $T$  after reaching complete cure.

The DMA degree of cure curves shown in Fig. 17A reveals that the rate and degree of “mechanical cure” vary dramatically with the cure temperature. These differences carry important kinetic information about the cure process, information that forms the basis for generating mathematical models of the cure process. By applying a time-temperature superposition method developed by Prime [53], the data from the isothermal cure curves at several different isothermal temperatures can be shifted to form DMA degree of cure mastercurves.

Based on the shift factor required to superimpose the data of Fig. 17A, the activation energy for the epoxy-polyester cure reaction in this example was estimated at 77.4 kJ/mol. As the DMA mastercurve in Fig. 17B shows, the superposition of data to times at 191°C is very good. The key advantage in applying reaction kinetics analysis in dynamic mechanical analysis (and other applicable techniques) is efficiency: a few experiments can provide as much information about the cure behavior as far more extensive laboratory work under many

different baking conditions. For example, in Fig. 18, simulated DMA degree of cure curves were generated at three bake temperatures and compared with the DOC at minimum impact resistance. The time required to reach a minimum performance level varies considerably; at 150°C, the coating fails to reach the minimum DOC even after 90 min. At 177 and 204°C, minimum DOC is reached after roughly 15 and 30 min, respectively. Obtaining the same information by a conventional experimental approach would require a considerable amount of time and effort in the laboratory. Moreover, techniques like the DMA TTS methods described here can predict the time required to reach a specified level of performance for any isothermal cure schedule.

## COMBINED TECHNIQUES IN PROBLEM SOLVING

Thermal techniques usually reserved for routine analysis and characterization or research support are also useful for solving problems that arise in process or production. Because problems in manufacturing present unusual experimental difficulties, solving them usually requires several methods for adequate characterization. A solitary piece of evidence, whatever the quality, usually needs corroborating information from other sources. Multiple techniques are particularly valuable in settling financial or legal claims where the need for undisputable evidence becomes preeminent. In the example described below [54], quality control tests in manufacturing indicated that container coatings sprayed on the interior of aluminum beverage cans were improperly cured, the cus-

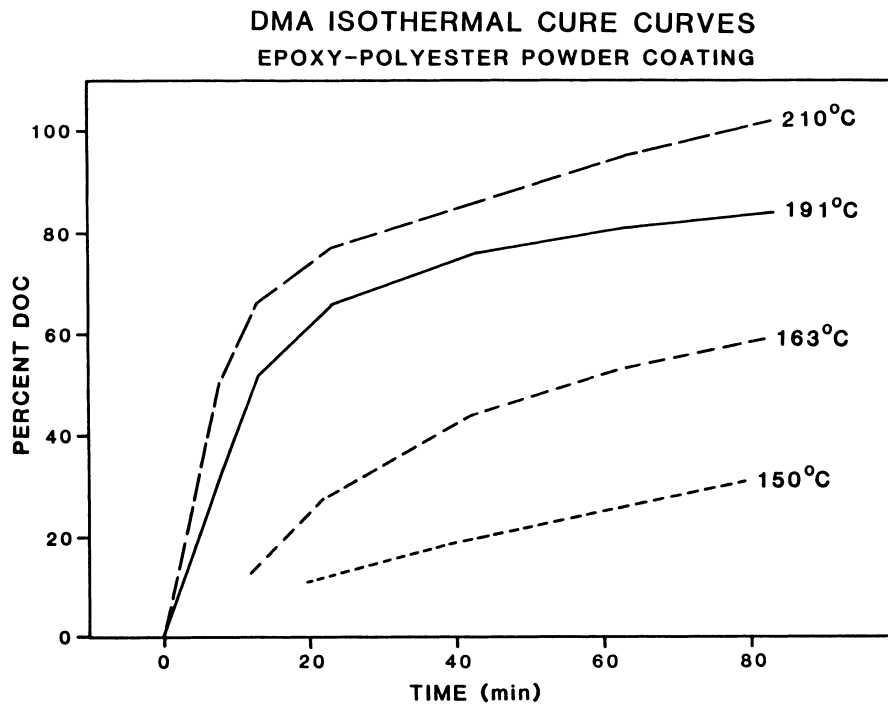


FIG. 17A—Epoxy polyester powder coating degree of cure curves.

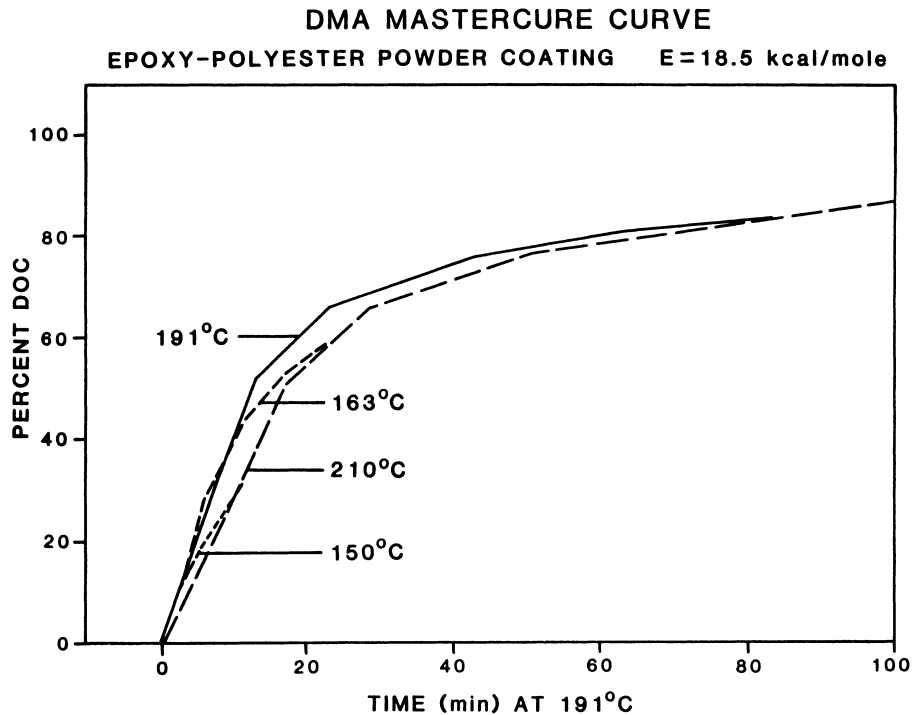


FIG. 17B—Epoxy polyester powder coating DMA mastercurves for cure at 191°C and an activation energy of 18.5 kcal/mol.

toomer attributing the cure problem to errors in the synthesis or formulation of the coating.

Four analytical techniques were required to adequately characterize various coating materials and pinpoint the cause of the problem. Compositional differences were assessed by FT-IR; morphological characteristics were ob-

served with scanning electron microscopy (SEM); DSC was used to assess differences in thermal behavior; and relative cure kinetics were measured using DMA. Each of the analyses revealed that differences between the problem coatings and other materials—either laboratory standard or production line standards—were not due to differences inherent in the

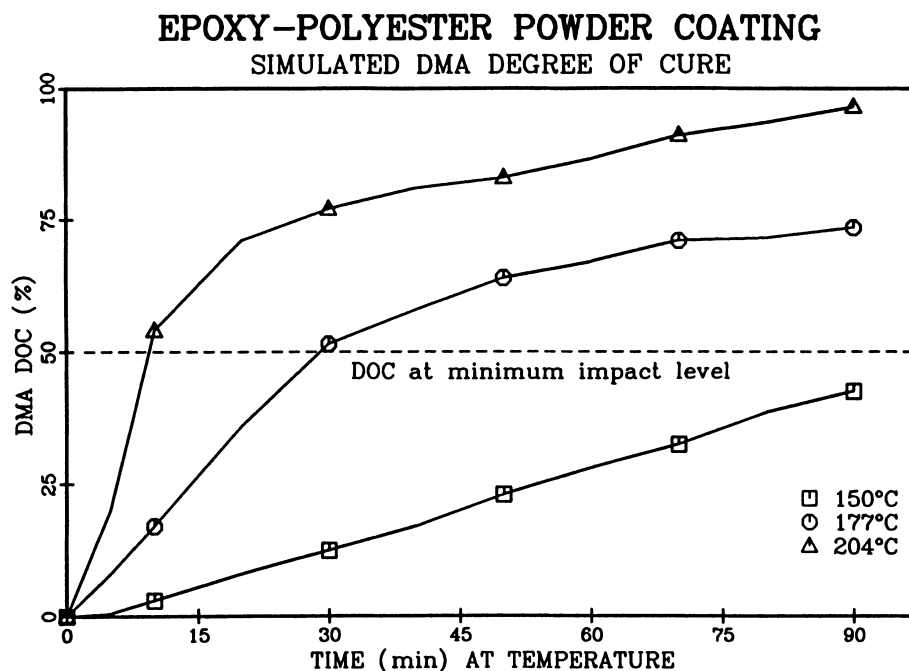


FIG. 18—Predicted time to minimum acceptable impact resistance at three isothermal bake temperatures.

chemistry of the coatings or formulation. Instead, these tests revealed that oven temperatures were probably too low to properly cure the coatings. After raising the oven temperature a few degrees, all of the coatings passed the QC test. Figure 19 compares the DSC heat flow characteristics of a

properly cured standard with curves of the problem coating before and after rebake. The key feature shown in this figure is a weak endotherm, apparently related to the level of cure in the problem coating. After rebake, this endotherm disappears and the thermal behavior of the problem coating is virtually

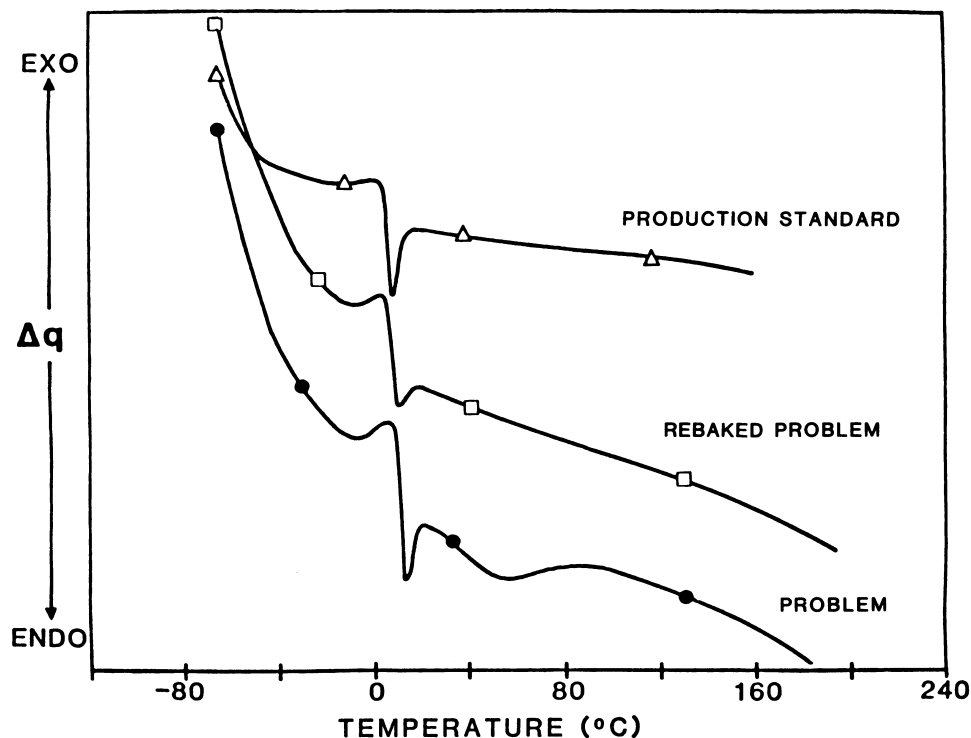


FIG. 19—Comparison of the DSC heat flow characteristics of a production standard, a problem coating, and the rebaked problem coating ( $\Delta q$  = heat flow).

identical with that of the properly cured coating. Similar comparisons using FT-IR to follow changes in reactive sites during cure showed that the "good" and "bad" coatings were virtually indistinguishable (provided that their thermal histories were the same). In fact, the results obtained from each of the instruments led to the same conclusion: when the problem coating was rebaked, it was virtually identical to the properly cured material. Taken together then, these results showed that the manufacturing problem was unrelated to the coating's chemistry. Instead, QC failures were caused by oven temperatures set too low to properly cure the coating.

## SUMMARY

Thermal analysis occupies a unique place in research and development. In most instances, the utility of an analytical technique is strictly limited by its output. For example, spectroscopic tools like NMR or IR tend to be viewed as stand-alone operations that provide a specified result. TA differs from other analytical operations because the instruments offer greater versatility. In fact, thermal analysis is generally recognized as a broad technology encompassing many instruments and many more applications. Depending on the need, the results delivered by TA can range from the straightforward, like Tg's, to the complex, like reaction kinetics parameters.

TA realizes its greatest value, however, when more than one instrument is focused on a research or production problem. In combination, these instruments can provide tremendous insight into the relationship between formulation, processing, and the ultimate performance of material, often clarifying hard-to-understand relationships [55]. When applied throughout the product development cycle, these instruments can reduce product development time, manufacturing costs, and, in the end, help shape the best possible product.

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