THERMAL ANALYSIS OF POLYMERS

Introduction

*Thermal analysis* is defined by the International Confederation of Thermal Analysis and Calorimetry (ICTAC) (1,2) as “a group of techniques in which a property of a sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed.” In practice, the temperature of the oven that contains the sample actually is programmed, while the temperature of the sample in some cases may differ from the programmed temperature. Exothermic or endothermic reactions or phase transitions in the sample subjected to the programmed temperature variation may cause variations in the temperature between the sample and oven up to several degrees.

The more common thermal analysis (TA) methods are listed in Table 1 (3). Acronyms used for the techniques are included in the right-hand column. The present discussion will be limited to the major techniques that are used to characterize polymer samples. These are differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetry (TGA), thermomechanical

<table>
<thead>
<tr>
<th>Property</th>
<th>Technique</th>
<th>Acronym</th>
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<tbody>
<tr>
<td>Mass</td>
<td>Thermogravimetry</td>
<td>TGA, TG</td>
</tr>
<tr>
<td>Apparent mass*</td>
<td>Thermomagnetometry</td>
<td>TM</td>
</tr>
<tr>
<td>Volatiles</td>
<td>Evolved gas detection</td>
<td>EGD</td>
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<td></td>
<td>Evolved gas analysis</td>
<td>EGA</td>
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<td></td>
<td>Thermal desorption</td>
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<td>Radioactive decay</td>
<td>Emanation thermal analysis</td>
<td>ETA</td>
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<tr>
<td>Temperature</td>
<td>Differential thermal analysis</td>
<td>DTA</td>
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<tr>
<td>Heat* or heat flux*</td>
<td>Differential scanning calorimetry</td>
<td>DSC</td>
</tr>
<tr>
<td>Dimensions</td>
<td>Thermodilatometry</td>
<td>TD</td>
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<tr>
<td>Mechanical properties</td>
<td>Thermomechanical analysis</td>
<td>TMA</td>
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<td></td>
<td>Dynamic mechanical analysis</td>
<td>DMA, DMTA</td>
</tr>
<tr>
<td>Acoustical properties</td>
<td>Thermosonimetry (emission)</td>
<td>TS</td>
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<tr>
<td></td>
<td>Thermoacoustimetry (velocity)</td>
<td></td>
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<tr>
<td>Electrical properties</td>
<td>Thermoelectrometry (resistance)</td>
<td>DETA, DEA</td>
</tr>
<tr>
<td></td>
<td>(voltage)</td>
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<td></td>
<td>(current)</td>
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<td></td>
<td>(dielectric)</td>
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<tr>
<td>Optical properties</td>
<td>Thermooptometry (spectroscopy)*</td>
<td>TPA</td>
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<td></td>
<td>Thermoluminescence (emission)</td>
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<td></td>
<td>Thermomicroscopy (structure)</td>
<td></td>
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<tr>
<td></td>
<td>Thermoparticulate analysis</td>
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</tbody>
</table>

*From Ref. 3.

*Change induced by an imposed magnetic field gradient.

*Power-compensated DSC.

*Heat flux DSC.

*Absorption, fluorescence, Raman, etc. Nonoptical forms of spectroscopy, eg, NMR, ESR, Mössbauer, etc, are also applicable.
analysis (TMA), dynamic mechanical analysis (DMA), and dielectric analysis (DEA). The most popular technique for polymer applications is DSC followed by TGA (along with its derivative, DTGA). The use of the other methods is not as widespread as DSC and TGA but is gaining in popularity. The realization of the potential for TMA as a valuable tool for polymer characterization is comparatively recent. DMA and DEA were originally developed by rheologists over 50 years ago and have been adopted by thermal analysts more recently.

In addition to the individual techniques cited above, there are situations where individual samples are subjected to a common atmosphere and thermal environment. This is referred to as a concurrent analysis. An example of this is the combined DTA and TGA measurement, where two separate measurement devices
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share the same oven. In some cases two or more measurements are performed on the same sample. There is also the possibility of interfacing several techniques, such as TGA combined with some form of evolved gas analysis such as gas chromatography, Mass Spectrometry (qv), or infrared spectroscopy (or some combination of these) (see CHROMATOGRAPHY, AFFINITY; VIBRATIONAL SPECTROSCOPY). This situation is referred to as ‘coupling’ or a coupled technique. Since the possibilities for interfacing several analytical techniques are quite large, concurrent or coupled techniques will not be considered further in this presentation.

Prior to the advent of DSC (ca 1964–65), DTA was first used in the field of geology to study clay mineralogy and pyrometry. The evolution of DSC has its origins in DTA, driven by applications in polymers and the timely development of techniques, instruments, and advanced software. In recent years, DSC has largely supplanted DTA for use in polymers, except for applications at high temperatures. Most commercial DSC instruments have a temperature range from $-150^\circ$C up to $750^\circ$C, which is quite adequate for most polymer applications.

**Differential Thermal Analysis**

**Description of the Method.** As shown in Table 1 and Figure 1, DTA measures the differential temperature between a sample and a reference pan, which are closely matched thermally and arranged symmetrically within the oven. As the sample goes through the programmed dynamic temperature change, there is no temperature difference until the sample undergoes an exothermic or endothermic chemical reaction or change of physical state. In the case of an exotherm, the sample’s temperature will increase, while in the case of an endotherm, it will decrease. In either case, the thermal event will be recorded as the sample temperature departs from the baseline and then returns to the baseline when the reaction or transformation is complete. Also, a change in the heat capacity of the sample will show as a change in slope (eg, Glass Transition (qv)) in the $\Delta T$ versus time or temperature plot. Modern DTA instruments generally use matched thermocouples as sensors, one each in contact with the sample or its container and the reference material or its container. The output of the differential signal is amplified and sent to a data acquisition system. Further details about DTA instrumentation and the appropriate experimental parameters can be found in several references by Wendlandt (4), Gallagher (Ref 5, Chapt. 1), and Wunderlich (Ref. 5, Chapt. 2). Some consideration of sample preparation, the effect of experimental parameters (eg, rate of heating and cooling), and methods for enthalpy and temperature calibration will be considered in the subsequent discussion of DSC.

**Applications of DTA for Polymers.** Table 2 (Ref. 5, Chapt. 1) describes some of the many applications of DTA and DSC. Both DTA and DSC can be used to determine the temperature of the transitions, cited in Table 2. However, the DSC peak area, in addition, gives quantitative calorimetric information (heat of reaction, transition, or heat capacity). DTA can only do so when calibration with a standard material allows the quantitative conversion of $\Delta T$ to heat flow and, ultimately, heat of transition ($\Delta H$) or heat capacity ($C_p$). Also, the response of DTA with increasing temperature may be affected by poor heat transfer in the
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Table 2. Some Applications of DTA and DSC to Polymers

<table>
<thead>
<tr>
<th>Application</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>Melting ranges</td>
<td>Release of strains</td>
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<tr>
<td>Rates of crystallization and reaction</td>
<td>Purity determination</td>
</tr>
<tr>
<td>Degree of crystallinity</td>
<td>Quality control</td>
</tr>
<tr>
<td>Glass-transition phenomena</td>
<td>Phase diagrams</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>Energy storage</td>
</tr>
<tr>
<td>Enthalpy of transitions</td>
<td>Hazards evaluation</td>
</tr>
<tr>
<td>Identification—Fingerprints</td>
<td>Mesophase transitions</td>
</tr>
<tr>
<td>Thermal and oxidative stability</td>
<td>Nucleation of crystals</td>
</tr>
<tr>
<td>Analysis of copolymers and blends</td>
<td>Catalysis</td>
</tr>
<tr>
<td>Nucleation phenomena</td>
<td>Thermal conductivity</td>
</tr>
</tbody>
</table>

system, detector sensitivity, etc (4). For these reasons, when there is a choice between DSC and DTA, DSC is the preferred method. The illustrations shown below for applications of DSC in characterization of polymers also generally apply for DTA, with the limitations mentioned above. Therefore, DTA applications will not be considered here. Illustrations of polymer applications for DTA can be found in the Thermal Analysis section by Bacon Ke (6) in the previous edition of this encyclopedia.

**Differential Scanning Calorimetry**

**Instrumentation.** The development and introduction of DSC in 1964 (7) was a major innovation in thermal analysis. Several competitive commercial instruments were developed shortly afterward. Basically, there are two types of DSC instruments. The Perkin-Elmer version is called the “power compensation” DSC. Zahra and Zahra (8) reviewed a recent version of this type of DSC instrumentation. Figure 2 provides a schematic representation of the power compensation DSC.

The concept of operation of this instrument is based on keeping the temperature of R and S the same. This is achieved by placing the temperature sensors (platinum resistance thermometers) in a bridge circuit. Any change in temperature in either the sample or in the reference (by virtue of any exo- or endothermic event) is immediately compensated for by an equivalent amount of current flow required to drive a heater to keep them at the same temperature. Thus, the integral of the power input during the transition (or the heat capacity change) is equal to the energy difference ($\Delta H$) supplied to the sample or the reference during the particular event. The event would be endothermic or exothermic depending on whether the current travels to the sample or the reference pan, respectively. This results in an exothermic peak pointing downward and an endothermic peak pointing upward. This is in conformity with the thermodynamic convention, but differs with the sign convention for the DTA and the DSC “heat flux” for instruments made by other manufacturers, as discussed below. For DTA,
ICTAC (2) recommends plotting “an upward deflection as a positive temperature differential and a downward deflection as a negative temperature differential with respect to the reference.” In other words, exo is upward and endo is downward.

The second type of DSC unit operates in a “heat flux” mode. This type of instrument is offered by TA Instruments, Mettler-Toledo, Setaram, Netszch, and other manufacturers. Its operation is similar to that of DTA (i.e., it generates a $\Delta T$ signal). However, the associated hardware and software, carefully integrated into the system, quantitatively converts $\Delta T$ to $\Delta H$ and compensates for other deficiencies, such as the temperature dependence of thermal transport and sensor sensitivity. Figure 3 shows two types of heat-flux calorimeters along with a schematic diagram taken from Boerio-Goates and Callanan (9). Figure 3a represents the Boersma-type instrument used by TA Instruments. In this unit, single thermocouples are in good thermal contact with the sample and the...
Fig. 3. Representation of a two heat-flux calorimeter showing (a) Boersma thermocouple placement and (b) the Tian–Calvet design. The schematic diagram (c) is appropriate for analysis of the response of both types of calorimeters. Symbols in (c) are: subscript T refers to temperature, R refers to reference; the temperatures of the block, sample, container, reference, and reference containers given by $T_B, T_{SC}, T_R, T_{RC}$, respectively; capital R refers to heat transfer resistance in the instrument (9).

reference holders. In the Tian–Calvet-type calorimeter, shown in Figure 3b, a thermopile is used. The latter tends to give greater temperature sensitivity and better temperature averaging over the entire sample and reference containers. The schematic representation in Figure 3c notes the temperatures and thermal resistances that are necessary for mathematical analysis of the heat-flux DSC. The analysis is described by Wunderlich (5). Each type of DSC gives satisfactory enthalpy data (10) with an accuracy of around 1–2%. Some heat-flux DSC instruments can operate at temperatures up to 1500°C, while the power-compensation instrument operation is limited to 725°C.

**Calibration and Standards.** Thermal analysis methods are not absolute and calibration is needed to record the correct abscissa value of temperature $T$
(in Kelvin) and time \( t \) (in seconds or minutes). On the ordinate, calibration is necessary for the amplitude of deflection, \( \Delta T \), expressed as the difference in temperature (in Kelvin) for DTA or as heat flux, \( dQ/dT \) (in joules per second or watts) for DSC. Each instrument manufacturer provides methods and standard materials for these calibrations. In addition, ICTAC, in collaboration with the National Institute of Standards and Technology (NIST), has developed a series of materials as calibration standards for DSC/DTA. These reference materials can be used to calibrate both the temperature scale (K, abscissa) and heat flow (J/g, ordinate) on the basis of the integrated area under the curve. Figure 4 shows the heat flow–temperature relationship for various solid–solid and solid–liquid melting standards. Table 3 lists the solid\(_1\)-to-solid\(_2\) transitions, melting points, and Curie temperatures of various pure metals, and also their transition enthalpies (J/g) (11).

Figure 5 illustrates temperature calibration curves for both DTA/DSC and TGA using high purity nickel as a magnetic material (Curie point = 358.4°C). Unlike \( T_m \), the Curie point temperature is practically unaffected by the changing of the heating rate between 1 to 20°C/min.

Hakvoort (16) and also Della Gatta and Barczynska (17) advocate certain solid-state first-order transitions for use as subambient temperature standards. For relatively low temperature ranges, such as the glass transitions (\( T_g \)) for elastomers, Tan and Sabbah (18) have proposed the melting transitions of various organic compounds. Certified reference materials for heat capacity calibration, which are recommended by International Union of Pure and Applied Chemistry (IUPAC), are also available (Ref. 5, pp. 46 and 353–356). Two ASTM standards

![Fig. 4. Typical enthalpy calibration curve for DSC.](image)

- Salt (Solid\(_1\)-solid\(_2\) standard)
- Metal (melting standard) (14)
Fig. 5. Thermomagnetometry (TM)/DTA curves for accurate determination of $T_c$ for magnetic materials (15).

document procedures for temperature (ASTM E967) and heat-flow (ASTM E968) calibration in DSC.

**Operating Parameters for DSC/DTA.**

**Sample Size.** In order to avoid temperature gradients inside a sample, a small sample size is preferred. A small sample size also gives better resolution.

On the other hand, sensitivity of the instrument increases with increasing sample size. The choice of sample size for DSC/DTA depends on the

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature, °C</th>
<th>Enthalpy, J/g</th>
<th>Material</th>
<th>Temperature, °C</th>
<th>Enthalpy, J/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>$-38.8344$</td>
<td>$11.5$</td>
<td>Cyclohexane</td>
<td>$-83.1$</td>
<td>Unavailable</td>
</tr>
<tr>
<td>In</td>
<td>$156.5985$</td>
<td>$28.42$</td>
<td>KNO$_3$</td>
<td>$127.7$</td>
<td>$50.48$</td>
</tr>
<tr>
<td>Sn</td>
<td>$231.928$</td>
<td>$59.2$</td>
<td>KClO$_4$</td>
<td>$299.5$</td>
<td>$99.32$</td>
</tr>
<tr>
<td>Pb</td>
<td>$327.502$</td>
<td>$23.16$</td>
<td>Ag$_2$SO$_4$</td>
<td>$412$</td>
<td>$59.85$</td>
</tr>
<tr>
<td>Zn</td>
<td>$419.527$</td>
<td>$112.0$</td>
<td>SiO$_2$</td>
<td>$573$</td>
<td>$12.1$</td>
</tr>
<tr>
<td>Al</td>
<td>$660.323$</td>
<td>$400.1$</td>
<td>K$_2$SO$_4$</td>
<td>$583$</td>
<td>$48.49$</td>
</tr>
<tr>
<td>Ag</td>
<td>$961.78$</td>
<td>$104.7$</td>
<td>K$_2$CrO$_4$</td>
<td>$665$</td>
<td>$51.71$</td>
</tr>
<tr>
<td>Au</td>
<td>$1064.18$</td>
<td>$63.7$</td>
<td>BaCO$_3$</td>
<td>$810$</td>
<td>$89.00$</td>
</tr>
<tr>
<td>Cu</td>
<td>$1084.62$</td>
<td>$205.4$</td>
<td>SrCO$_3$</td>
<td>$925$</td>
<td>$133.23$</td>
</tr>
</tbody>
</table>

*International Temperature Scale 1990 for temperatures, and Ref. 12 for the enthalpies.
*NBS–ICTA Certificates GM-758, GM-759, GM-760 for the recommended temperatures, and Ref. for the enthalpies.
*Downgraded to a secondary temperature point.
composition of the sample. For pure polymers, 3–10 mg is sufficient. For heterogeneous materials, such as blends and filled polymers or those containing several other compounding ingredients (such as elastomer vulcanizates), larger samples in the range of 10–20 mg may be necessary. However, for characterization of all materials in an air or oxygen environment, thin samples weighing only 0.2–0.5 mg are recommended in order to minimize diffusional effects with respect to oxygen or air, inhibit secondary reactions, and improve reproducibility. In the case of heterogeneous materials it is advisable to run multiple samples in order to verify that the data are representative of the composition.

**Sample History.** A factor that is characteristic of polymers is the dependence of morphology on thermal history. Significant variations in the degree of crystallinity as well as temperatures for glass transition ($T_g$), crystallization ($T_c$), and crystalline melting ($T_m$) can be obtained by varying the crystallization and annealing temperatures, or by changing cooling and heating rates. Additional types of sample history may be due to the viscoelastic character of the polymer. Elastomer samples that have been pressed, molded, or extruded may exhibit appreciable elastic “memory,” which eventually may result in severe distortion of the sample during the TGA, DSC, and DMA experiments. This would result in anomalous data. Another type of time-dependent sample history variation can be encountered with thermoplastic block copolymers. Here changes in dimensional stability and/or polymer transition temperature may occur because of changes in the morphology of the material during the thermal measurement. This might result from changes in the phase distribution resulting from aggregation of the hard or soft block segments. A further complication is physical aging or enthalpy relaxation that occurs in the amorphous phase due to the tendency of a polymer in a nonequilibrium state to spontaneously shift toward the equilibrium state. This is a complex subject that is not considered here but is covered in some detail by Chartoff in Reference 5.

In order to obtain a representative DSC curve for the polymer sample that is consistent and reproducible, it is necessary to destroy the prehistory. This is achieved by preheating the sample above the crystalline melting temperature in an inert atmosphere, holding it there for a few minutes (generally, 5 min) and then cooling slowly to the start temperature. If the crystallization rate is slow, it may be necessary to hold the polymer (ie, anneal) at a temperature below the melting point for some time in order for crystallization to go to completion.

In certain cases, whenever a special kind of prehistory is imparted to a polymer (eg, either through processing or aging, such as in fiber and film processing from the melt), it is important to study the prehistory. Here it may be desirable *not* to destroy the prehistory because the DSC response of the material may be correlated with a process parameter, thus extending the usefulness of the DSC curve. In this case, one should always record the first heat DSC/DTA curve followed by a second run using the reheat procedure noted above.

**Base Line.** Selecting a proper base line for integrating the area under the curve is essential for enthalpy determinations. In the absence of detailed information about overall error in different alternative modes, a simple straight-line approach is adequate. However, for partial area measurements in kinetics, a more accurate base line may be needed. The following texts may be consulted for further information on this topic: Wendlandt (4), Brown (19), and Wunderlich (11).
Many modern instruments have the ability to manipulate the base line. In the case of irreversible transformations without any weight loss, a simple rerun of a sample (after the transformation), under the same conditions should give a suitable base line. All current computerized instruments can subtract one base line from another that is generated under identical experimental conditions.

**Thermal Transport.** Heat transfer to the sample can be affected by the following factors: (1) physical arrangement of the sample and reference relative to the furnace; (2) the choice of sensor, its size and position; and (3) the type of construction materials. These factors determine the thermal coupling. They also influence the shape and size of the peak for a thermal event. The better the thermal coupling between the sample and the reference, the smaller the original $\Delta T$ signal and the faster the return to the base line, thus improving resolution. A higher thermal conductivity environmental gas, such as helium, will result in better thermal coupling. Placing a metal lid on the sample pan also markedly improves the thermal properties of the system by helping to press the sample into good contact with the pan and reducing heat flow to the environment.

**Effect of Heating Rate.** The thermal lag between the sample and the sensor increases as the heating rate increases and, generally, the resolution of a transition (or other thermal event) decreases. However, the amplitude of the $\Delta T$ signal increases with heating rate because the transition takes place in a shorter period of time and the rate of change is greater. With modern instruments, amplification of the $\Delta T$ signal at a lower heating rate is not a problem, but it increases the signal-to-noise ratio. Therefore, compromises must be made. Typical heating rates for DSC experiments are in the 10–20°C/min range. For unknown polymer samples, a range of heating rates with different amounts of sample should be explored. This should provide information on the optimum conditions for detection and resolution of minor thermal events and would be a background study for establishing a routine procedure for subsequent analyses. The effects of different parameters on resolution and sensitivity are summarized in Table 4 (Ref. 5, p. 87).

### DSC Applications in Polymers

The numerous applications of DSC in characterizing polymeric materials are quite varied. Therefore, it is only possible to cast a glimpse on the subject. Figure 6 shows a schematic DSC curve (20) for a pure polymer as it is progressively

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**Table 4. Compromises in Operation and Construction for DTA and DSC**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Maximum resolution</th>
<th>Maximum sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample size</td>
<td>Small</td>
<td>Large</td>
</tr>
<tr>
<td>Heating rate</td>
<td>Slow</td>
<td>Fast</td>
</tr>
<tr>
<td>Sample–reference</td>
<td>Linked</td>
<td>Isolated</td>
</tr>
<tr>
<td>Particle size</td>
<td>Small</td>
<td>Large</td>
</tr>
<tr>
<td>Atmosphere&lt;sup&gt;a&lt;/sup&gt;</td>
<td>High conductivity</td>
<td>Low conductivity</td>
</tr>
</tbody>
</table>

<sup>a</sup>In the absence of any reaction.
heated from a low temperature to a high temperature in an oxidative (A) or inert (B) atmosphere. The actual temperature, for a given polymer to undergo all of the thermal events shown in Figure 6, depends on the structure of the polymer. For an elastomer, a low temperature transition (glass-transition temperature $T_g$) may be as low as $-140^\circ C$, whereas for a thermoplastic polymer, $T_g$ values of room temperature or higher may be more common. As noted before, the DSC experiment should be started at a temperature at least 20–50°C lower than the region of interest and continued to at least 20°C higher than the highest transition temperature. The elevated temperature at which most carbon-chain polymers degrade is usually less than 500°C.

Starting from the lowest temperature, the first discontinuity observed is the glass transition, which appears as a shift of the base line corresponding to the heat capacity difference of the sample before and after the transition. There are various methods to mark the exact location in the curve where the glass-transition temperature $T_g$ is recorded. This will be discussed below. The magnitude of base line shift ($\Delta C_p$) during the glass transition is related to the concentration of amorphous chains in the sample and is affected by other factors such as molecular mobility and free volume.

As the temperature increases, there may be a cold crystallization peak ($T_c$, exotherm), followed by a crystalline melting peak ($T_m$, endotherm). The intensity of the cold crystallization peak depends on the prehistory of the sample. It will not be present at all if the sample were cooled under controlled conditions from the melt state or if it were annealed at a fixed temperature below $T_m$ so as to complete the crystallization process. If the sample is heated above $T_m$ and then cooled slowly to a low temperature, and scanned again, the enthalpy or the area under the melting curve will relate directly to the amount of crystalline material in the
polymer or the degree of crystallinity. Up to this point, the transitions mentioned are due to physical changes and they are reversible. Physical transitions are not accompanied by any weight change and are not affected by the environment (nitrogen or oxygen). Thus, they cannot be monitored using TGA, since there is no weight loss involved.

At a still higher temperature (150–220 °C), if the polymer is an elastomer, formulated with all the vulcanizing ingredients or uncured thermosetting type monomer, an exotherm should occur indicating the curing reaction (not shown in Figure 6). DSC enthalpy determination (from the area under the exotherm) is one of the methods for determining the degree of cure of an elastomer formulation or a thermoset and can be used as a quality control tool.

At still higher temperatures (250–500 °C), the polymer undergoes degradation, resulting in main-chain scission, cross-linking, cyclization, and loss of volatile fragments. In an inert atmosphere, the degradation pattern may be endothermic, exothermic, or both, whereas in oxygen or air, it is always exothermic. As expected, degradation occurs at a much lower temperature in oxygen than in nitrogen. The DSC degradation patterns in nitrogen and oxygen have been used to identify many polymers (21). Many authors, including Goh (22) and Savascı and Baysal (23) have attempted to use oxidation exotherms to characterize the oxidative stability of elastomers, and, subsequently, to evaluate the effectiveness of added antioxidants. DSC curves in the degradation regime may tend to be erratic because of the loss of mass that may occur during the degradation event.

**Glass-Transition Temperature.**

*Specifying Tg by DSC.* All amorphous polymers become stiff and ultimately brittle like a glass, if sufficiently cooled. The temperature region where the physical transition from a rubbery to a glassy state takes place is called the “glass transition.” It is characterized by a step change in \( C_p \). As shown in Figure 7, the glass transition covers a wide range of temperature (10–15 °C for pure, uncross-linked polymers and wider for blends, filled, and cross-linked polymers). A defined point in this temperature range is called the glass-transition temperature or \( T_g \).

Figure 7 shows five characteristic temperatures associated with a glass transition on the DSC curve. All five have been cited in various places in the literature as \( T_g \), often without mention of the specific location actually picked (24). The assignment of \( T_g \) by thermal analysis methods was the topic of a recent ASTM symposium (25). \( T_o \), the “onset” temperature, defines the point at which the first deviation from the base line on the low temperature side is observed. \( T_o \) is very subjective and often difficult to determine because of the base line slope; and it is not reproducible. \( T_e \) or \( T_{eo} \) (extrapolated onset, also called the fictive temperature) is the temperature at the intersection of the extrapolated base line and tangent taken at the point of maximum slope. It is generally reproducible and is the most quoted value in many early publications on thermal methods. \( T_{0.5} \), the endotherm half-height (also called half-vitrification) is the temperature preferred in recent years for specifying \( T_g \). The autoanalysis feature available with all modern thermal analysis equipment makes this determination easy and reproducible. It has better reproducibility than the extrapolation method and locates a temperature where the thermal transition has approximately reached the
Fig. 7. Representative curve of heat flow versus temperature in the region of the $T_g$ of a polymer: $T_o$, temperature of departure from the base line; $T_e$ or $T_{eo}$, temperature of intercept of extrapolated base line and tangent to steepest slope; $T_{0.5}$, temperature of 50% transition ($A = B$); $T_p$, temperature of maximum slope (peak of derivative plot); $T_f$, temperature at completion of the transition (24).

inflection point. ASTM E1356 and ASTM D3418 recommend either $T_e$ or $T_{0.5}$ for specifying $T_g$. Wunderlich (Ref. 5, p. 278) advises that $T_g$ should be measured as the sample is progressively cooled, rather than heated. The advantage here is that the sample is in thermal equilibrium at the start of the measurement and enthalpy relaxation, often encountered in $T_g$ measurements, is avoided. However, instrumental drawbacks, such as precise control of the cooling rates in some DSC models, preclude general use of cooling curves for determining $T_g$. If $T_g$ is obtained by progressive heating of a cooled sample, it is advisable to cool the sample somewhat faster than the subsequent heating rate to avoid enthalpy relaxation. This is also discussed by Wunderlich (5). The heating or cooling rate and the location on the DSC curve where $T_g$ is taken always should be specified along with the reported $T_g$ value.

Another method for locating $T_g$ is by taking the derivative of the DSC glass-transition curve. (The acronym DerDSC for “derivative DSC” is used here.) The derivative curves exhibit a peak corresponding to the maximum slope of the endothermic step in $C_p$ accompanying $T_g$. In Figure 7, $T_p$ is very close to $T_{0.5}$, the midpoint value. This is illustrated in Figure 8 for natural rubber (26). Note the small endotherm at the high temperature end, presumably due to enthalpy relaxation. The derivative curves may also be helpful in locating multiple transitions close in temperature and not resolved by the $T_g$ curve (Ref. 25, p. 229). The disadvantage of this method is the high signal-to-noise ratio for the DerDSC curves.
For amorphous thermoplastic polymers, $T_g$ at the extrapolated onset is technically more significant, since it defines the initial temperature for the loss of structural properties (e.g., modulus) as the polymer softens through the glass-transition region. Thus, it defines both a low temperature limit for the processing of amorphous thermoplastic polymers and an upper use temperature. For elastomers, the temperature for useful elastomeric properties lies above the glass-transition region, (to the right of the $T_g$ curve) shown in Figure 7. Therefore, $T_f$, the temperature at the completion of the glass transition, should be technically more significant (26). If the elastomer is cooled beyond this point it enters the glass-transition region and starts losing its elastic properties, becoming progressively stiffer as the temperature decreases. As noted above, ASTM E1356 describes the test method for determining the glass-transition temperature by DSC or DTA.

**Degree of Cure Using $T_g$.** For many thermosets, $T_g$ can be correlated with the conversion or degree of cure (Ref. 5, Chapt. 6). Therefore, simultaneously with the heat of reaction, measured by enthalpy, $T_g$ can be used as a measure of the degree of cure. In the final stages of cure, where $T_g$ is actually the more sensitive measure, it may be preferred to the residual heat of reaction, $\Delta H_1$, as a measure of the degree of cure. This may happen when the glass transition immediately precedes the small residual exotherm. This is illustrated in Figure 9 (27) for epoxy–anhydride samples, previously cured to apparent completion at different temperatures. Note that the exotherms are facing downward, as would be expected for a power compensation DSC instrument; $\Delta H_c$ is the exothermic heat of reaction for 100% conversion, expressed as heat per mole of reacting groups (kcal/mole or kJ/mole) or per mass of material (cal/g or J/g) at the time $t$. The fractional degree of conversion is given by

$$\alpha_l = \Delta H_l / \Delta H_c$$  \hspace{1cm} (1)
where $\alpha_1$ is the fractional conversion or extent of reaction and $\Delta H_1$ the heat generated up to time $t_1$.

The measurement of the degree of conversion by enthalpy measurement applies to elastomer cure also, since the vulcanization reaction is highly exothermic. Unlike for thermosets, $T_g$ is not a measure of degree of cure for elastomers. Sircar discusses this and numerous other aspects of the characterization of elastomeric materials using thermal analysis in chapter 5 of Reference 5.

**Melting in Semicrystalline Polymers.**

*Traditional DSC Methods.* Many commercially available thermoplastics [eg, polyethylene (PE), polypropylene (PP), poly(ethylene terephthalate) (PET), various nylons, and numerous others] and some elastomers [eg, polychloroprene, known commercially as neoprene (CR), cis-1,4-poly(butadiene) (BR), ethylene–propylene–diene polymer (EPDM)] are morphologically semicrystalline. These are virtually two-phase systems where a crystalline phase and an amorphous phase coexist. However, the crystalline phase and the amorphous phase are not completely homogeneous. The crystals generally are of different sizes and forms and the amorphous phase near the crystallite interfaces is constrained and less
mobile than the amorphous chains far from the crystallite boundaries. DSC is a useful tool for characterizing these semicrystalline materials.

Other important characteristics of Semicrystalline Polymers (qv) are that melting takes place over a range of temperatures (in some cases, over a range of 100°C or more) and supercooling always occurs, so that there is a hysteresis between the melting and crystallization cooling curves. Semicrystalline polymers melt at characteristic temperatures when heated in DSC. Wunderlich (Ref. 5, p. 277) describes reasons for designating the melting temperature \( T_m \) at different locations of the melting curve (Fig. 10). If there is a large temperature gradient within the sample, it has been observed empirically that the peak temperature often represents the actual melting temperature. Also, a sample with a broad melting range and a small melting rate (as are the semicrystalline polymers with crystals of different perfection, shape, and size) should be better characterized by its melting peak temperature, since \( T_p \) represents the temperature where the largest fraction of the sample melts. This is the most frequently quoted \( T_m \) for semicrystalline polymers. Lastly, the temperature for recovery of the base line, \( T_e \), is a function of the design of the instrument. For a polymer with a very broad melting range, the instrument lag becomes negligible and \( T_e \) would indicate the melting temperature of the most perfect, highest melting crystals of the sample.

Another important characteristic of melting for semicrystalline polymers using DSC is the enthalpy or the value of the heat of fusion, \( \Delta H_f \). It should be noted that the value of \( \Delta H_f \), determined by DSC, denotes only the amount of crystallinity present in the sample and not the inherent value of the enthalpy of fusion of a fully crystalline polymer, \( \Delta H_u \). Methods for determining \( \Delta H_u \) are described by Starkweather and co-workers (28). If the enthalpy of fusion of the fully crystalline polymer is known, the degree of crystallinity of an unknown polymer sample can be determined as follows:

\[
\text{Degree of crystallinity (\%) } = \left( \frac{\Delta H_f}{\Delta H_u} \right) \times 100
\]  

(2)
As in the case of the glass transition, another important item to be reported is the heating or cooling rate. Equilibrium melting should be independent of heating rate, but rarely do polymer crystals represent equilibrium crystals, nor do they melt in DTA or DSC under equilibrium conditions. Under such nonequilibrium conditions, the time scale of a first-order transition (such as melting) is an important experimental parameter. It should be noted again that the magnitude of the step change in the base line during the glass transition relates to the amorphous content of the polymer. Similarly, the magnitude (area) of the melting transition enthalpy relates to the degree of crystallinity of the polymer. The degree of crystallinity of a semicrystalline polymer is an important parameter that correlates with most major engineering mechanical properties including elastic modulus, strength, and elongation to break. DSC is the most efficient method for accurately measuring the degree of crystallinity.

**Modulated Differential Scanning Calorimetry.** A relatively recent development in DSC instrumentation allows heating or cooling a sample under a constant underlying rate while simultaneously superimposing a sinusoidally varying time–temperature wave. This is shown in Figure 11 for the modulated differential scanning calorimetry [MDSC, TA Instruments; Sauerbrunn and co-workers (29)]. As described below, the accepted name for this method has since been changed to modulated temperature DSC, or MTDS, after this term was introduced in 1996. A similar technology [dynamic DSC or step scan DSC (SCDSC) developed by Perkin-Elmer] is based on a series of isothermal holds, each followed by a linear heating segment (ramp) instead of the sinusoidal cycle of MTDS. Schawe (30) compares the two methods (MTDS versus DDSC) using the glass transition as an example. The results are virtually identical.

A major advantage of the MTDS technique and analysis is that the total heat flow rate can be separated into two other signals by deconvolution of the raw data (Fig. 11b). One of these is a reversible signal, in phase with the modulated heating rate, and the other a nonreversible signal out of phase with the modulated heating but dependent on the rate of heat flow. Examples of polymer thermal events that are nonreversible are molecular relaxation, cold crystallization, evaporation, thermoset cure, elastomer vulcanization, and decomposition. The utility of having two response components is demonstrated in Figure 11c for PET, where the glass transition and the melting endotherm are reversible but the endothermic enthalpy relaxation at $T_g$ and the exothermic cold crystallization are not. Another advantage of MTDS is that once the instrument is calibrated for the amplitude and period, heat capacity data can be obtained directly in the same run by measuring the modulated heat flow signal, and dividing by the amplitude of the heating rate.

An interesting analysis of a blend of PET/polycarbonate (PC), using MTDS, was reported by Hale and Bair (Ref. 5, p. 804) (Fig. 12). The conventional DSC curve (A) has all the indications of PET, but PC cannot be detected without the deconvoluted reversing curve (B) that indicates PC is present by virtue of its $T_g$ that occurs in the same temperature range as the cold crystallization of PET. Further confirmation of the presence of PC is obtained from the dynamic mechanical storage modulus (curve C). The dynamic modulus technique will be discussed later in this article.
In the MTDSC technique, $C_p$ (heat capacity) data from the convoluted MDSC is replaced with the term $C_p^*$, called a complex heat capacity. $C_p^*$ can then be further deconvoluted into an out-of-phase $C_p''$, and an in-phase ($C_p'$), component relative to the imposed temperature modulation. The vector sum of these components is equal to complex heat capacity, the data traditionally generated by MDSC. For most polymers, $C_p''$ is very small. In those cases, $C_p$ and $C_p^*$ will be virtually identical. However, a phase correction in MDSC should be relevant for time-dependent heat capacity phenomena. Aubochon and Gill (31) present a good comparison of MDSC and MTDSC with illustrations. The attention of
Fig. 12. Modulated DSC curve for Makroblend UT-400, an impact-modified polycarbonate/poly(ethylene terephthalate) blend. Curve A shows the conventional DSC curve; curve B shows the heat capacity extracted from the reversing component of the signal; curve C shows the modulus of the same material measured by DMA (Hale and Bair, in Ref. 5).

interested readers is also directed to the papers on MDSC and MTDSC presented at the 11th ICTAC conference (1996), and later published in three volumes of the *Journal of Thermal Analysis* (1997). NATAS, the North American Thermal Analysis Society, has sponsored symposia on MDSC at each of its meetings for the past several years.

**DSC Modifications and Simultaneous Techniques.** DSC and other thermal analysis instrumentation have undergone many modifications and developments in recent years. Among these innovations is the coupling of various methods. In this context the terms *parallel*, *concurrent*, and *simultaneous* should be defined. Parallel techniques use separate samples, each in its own unique thermal environment. Concurrent or combined techniques also use separate samples, but the experiment is carried out in a common atmosphere and thermal environment. Simultaneous techniques use the same sample in the same atmospheric and thermal environment. Such methods are increasing in popularity. While a detailed treatment of this topic is outside the scope of this discussion, a brief list will be presented in order to provide input for those new to the subject area. Interested readers should consult the chapter by Gallagher (5) and the additional references mentioned therein.

Some of the simultaneous instruments available commercially are as follows: TGA/DTA/DSC, TGA/DTA/FTIR, DTA(DSC)/EGA(EGD), and DSC/FTIR. Also, high pressure DSC and photo-DSC instruments are available commercially. In addition, individual researchers have used simultaneous DSC/XRD (X-ray diffraction), DSC/EGA/XRD, and DSC/TRXRD (time-resolved X-ray diffraction).
Experiments with parallel, combined, and simultaneous techniques help to affirm the conclusions drawn from a single technique and very often offer definitive clues to the actual mechanisms taking place during thermal analysis.

Thermal conductivities can be measured using DSC. Chiu and Fair (32) irreversibly modified a DSC cell to determine thermal conductivity. Sircar and Wells (33) developed a modification of this approach, which allowed the use of the same cell for conventional DSC work as well as for the measurement of thermal conductivity. Marcus and Blaine (34) discuss the possibilities for using MTDSC for measuring thermal conductivity.

Thermogravimetry

The terms, thermogravimetry (TG) and thermogravimetric analysis (TGA) are synonymous. Both ICTAC and International Union of Pure and Applied Chemistry (IUPAC) accept either of them. This is because of the early use and popularity of the term TGA, as well as an interest in avoiding verbal confusion with the glass transition $T_g$. There may also be potential problems with computer searching. Thermogravimetry involves the continuous recording of mass versus temperature or time as a sample is heated in a furnace with a controlled environment. The sample may be heated at a constant rate or held at an isothermal temperature. Madorsky (35) and Jellinek (36) authored major books dealing with thermogravimetry of polymers. The era of modern automated thermogravimetry started with the introduction of the electrobalance by Cahn and Schultz (37). Other competitors, such as DuPont, Mettler, and Perkin-Elmer, introduced their products in rapid succession.

Description of a TGA Instrument. The components of the instrument are the microbalance, the furnace, the programmer controller, and a computer or
data acquisition system. Typical arrangements of the components for TGA are shown in Figure 13. The sample can be linked to the balance in three different ways: (1) above the balance, (2) below the balance, and (3) beside the balance as a horizontal extension to the beam.

Arrangement 1 is the most common. However, arrangement 3 is actually preferred because it minimizes the heat effects of the furnace that may be encountered in arrangement 2 and is less influenced by the flow patterns of the gases within the balance and furnace chamber. It also lengthens the balance lever arm, increasing sensitivity, and minimizes the problem of condensation of volatiles on the sample support. In order to minimize thermal expansion of the balance lever arm, quartz is frequently the beam material of choice.

The Balance. Figure 14 shows a schematic of the Cahn electrobalance (38) most frequently used in thermogravimetry work (arrangement 1). A photodetection system monitors the beam position. If the beam moves from the horizontal, enough current flows to the torque motor to move the beam back to its original position. The restoring force generated by the current is proportional to the change in mass. A sensitivity of 1 $\mu$g is easily achieved. The sensitivity and total capacity of the balance have an inverse relationship. A commercial instrument with high sensitivity (ELCHEMA of Potsdam, New York) has a sensitivity of 0.1 $\mu$g and an operating range of up to 100 $\mu$g.

The Furnace and Controller. The heating elements of the furnace are most often resistance heaters. Nichrome and Kanthal elements are used for the temperature range up to 1000–1200°C. This range is sufficient for most polymer applications. Aluminum sample pans are often used for low temperatures up to 600°C. For higher temperatures, platinum pans are frequently used as sample containers. For higher temperatures in the range up to 1500–1700°C, molybdenum disilicide (Super Kanthal) or silicon carbide (Globar) is used for heating elements, and platinum or platinum alloys for sample pans. Ceramic refractories such as mullite or alumina are needed to contain the controlled atmosphere. Only a few manufacturers, such as Linseis, Netzsch, and Setaram, market instruments.

![Fig. 14. The Cahn electrobalance (19).](image-url)
Table 5. Major Factors Affecting Thermogravimetry

<table>
<thead>
<tr>
<th>Mass</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buoyancy</td>
<td>Heating rate</td>
</tr>
<tr>
<td>Atmospheric turbulence</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>Condensation and reaction</td>
<td>Enthalpy of the process</td>
</tr>
<tr>
<td>Electrostatic and magnetic forces</td>
<td>Sample, furnace, and sensor arrangement</td>
</tr>
<tr>
<td>Electronic drift</td>
<td>Electronic drift</td>
</tr>
</tbody>
</table>

for use above 1700°C. They are expensive and perform poorly below 300°C. Such high temperatures usually are unnecessary for polymers.

Most instrument manufacturers offer several furnace options in interchangeable modules to cover a broad range of temperatures. Thermal shock, oxidation, and vaporization shorten the life span of the resistance elements and refractories so that they may need occasional replacement. The higher the temperature of operation, the more severe this problem is. To enhance TGA instrument lifetime, Gallagher (5) recommends current limiting devices, thermocouple protection circuits and conservative ratings. Also, short times at elevated temperatures and less cycling to high temperatures will help. The use of dedicated computers and microprocessor chips has markedly improved the effective sensitivity and temperature control of modern instruments. Speyer (39) describes many of the fundamental considerations for the proper design of TGA equipment.

For checking uniform heating rates, the temperature \((T)\) versus time plot \((t)\) is suggested. Wendlandt (40) found that replacing \(T\) in the above plot with the derivative \(dT/dt\) shows temperature fluctuations better than those of the temperature versus time plot. For further details, refer to the chapter by Gallagher (5).

**Major Factors Affecting Thermogravimetry.** Mass and temperature are the two most important parameters that must be determined accurately for proper characterization of a material by TGA. Table 5 (Ref. 5, p. 24) shows all of the factors that need to be taken into account for accurate determination of either mass (left-hand side) or temperature (right-hand side). However, it is easier to deal with corrections for mass than it is for temperature. The following discussion summarizes these factors.

**Mass.** The factors that may affect mass determination are buoyancy, atmospheric turbulence, condensation and reaction, electrostatic and magnetic forces, and electronic drift. Buoyancy corrections arise because the sample is in a lighter gas environment as the temperature of the environment increases. This shows up as a greater weight for the sample. The correction for this is minimal and, except for most accurate or demanding work, it can be neglected. If needed, there are suggestions for both instrumental and software adjustments that will take care of the correction. Atmospheric turbulence depends on the specific gas, its flow rate and pressure, as well as geometrical considerations. Wendlandt (4) discusses these factors in detail and suggests necessary compromises.

Evolved volatile products may condense on the cooler parts of the sample suspension system, thus altering the measured mass loss. The direction of
flow of the evolved gases must be manipulated to protect the vulnerable parts of
the balance mechanism, temperature sensor, and furnace windings from chemi-
cal attack. Also, in case the TGA system becomes contaminated from the prod-
ucts of the high temperature decomposition, subsequent experiments (partic-
ularly at high temperature) may be affected. An easy solution for this is to
heat the system to around 600°C in an oxidizing atmosphere. This will elimi-
nate most organic condensation products. If there is a chemical reaction with a
component in the environment, there may be specific effects on the reversibil-
ity and the chemical equilibrium involved. Examples of this are the decompo-
sition of carbonates, sulfates, hydroxides, and hydrates in the presence of CO₂,
SO₃ and water, respectively. The partial pressure of the gases present will de-
terminate the extent of the respective reactions. Consequently, the degree of de-
composition will be determined by the ability to sweep away the decomposition
products.

Catalytic reaction of the sample pan with the environment can also af-
fect the environment. Moreover, potential reactions of a sample with the sam-
ple holder must be considered. For example, a silica crucible will lower the
decomposition temperature of CaCO₃ by about 600°C in the presence of the self-
generated atmosphere of CO₂. There is potential for reactions of materials such
as alkalis and alkaline earth carbonates to react with ceramic or metal parts of
the sample holder.

The form or packing of the sample is another factor that will determine ex-
cess of the degree of contact with gaseous environment and the rate of escape
of the volatile products. Thus, decomposition may be diffusion controlled and de-
pendent on the sample geometry instead of chemically controlled and dependent
only on the sample composition. Packing will also affect the thermal gradients in
the sample. Thus, results for a single “lump” of a sample, rather than a powder,
may differ.

Low humidity of the surroundings and purge gases can generate electro-
static forces that can cause the sample holder to be attracted to or even stick to
the nearest wall, thus disturbing the mass signal. This effect tends to be seasonal
(dry winter) and there are simple remedies, such as wiping glass surfaces with
conducting liquids or surfactants and providing a ground connection through thin
metallic film on the glass surface. If moisture can be tolerated, the gas stream can
be humidified to eliminate electrostatic charges or, if it is not too hot, the outer
wall surface can be wrapped with a moist covering. The electronic drift problem
usually is relatively minor and only becomes a problem for experiments lasting
for several hours.

Temperature. As mentioned above, accurate temperature control is more
of a problem in TGA than is weighing mass accurately. Referring again to the five
factors affecting accurate temperature measurement as listed on the right-hand
side of Table 5, geometrical placement of the sensor, the sample, and the furnace
are particularly important. The sample should be as near to the thermocouple as
possible in order to sense accurately the temperature of the sample, but should
not affect the measurement of weight. It should not undermine effective control
of the programmed rate of heating and cooling by virtue of the heating or cooling
generated by any exothermic and endothermic reactions that take place. Also, the
products of decomposition may have a corrosive effect on the thermocouple and
balance parts. Thus, these volatile products should not come in contact with system components. Some of these requirements are contradictory, and compromises must be made.

The most common configurations for the placement of the sample and the thermocouple are shown in Figure 15 (Ref. 5, p. 30). This emphasizes the contradictions in the above requirements and the uncertainty in measuring the actual temperature of a sample. Very often, thermal runaway reactions caused by highly exothermic processes (e.g., oxidative decomposition of polymers) show as foldback curves (where the temperature increases and then decreases as heat is released) in the mass or weight % versus temperature plot. There is no completely satisfactory remedy for this. Using a high thermal conductivity atmosphere (helium) reduces the response time for temperature control and permits better heat dissipation or absorption by the sample but cannot completely alleviate the problem. Also, at a high flow rate, the high thermal conductivity gas will increase the heat loss from the furnace causing an increase in the power level necessary to obtain the same temperature.

Sartorius-Werke GmbH developed a clever solution (41). Here the balance and the sample chamber are completely separate, linked magnetically with a simple suspension (Fig. 16), thus alleviating the problem of corrosive gases coming in contact with the balance mechanism. A modern version of this “Thermosuspension balance” is available from Netzsch.

A number of manufacturers supply TGA instruments capable of operation in high vacuum or high pressure. A TGA with a magnetic suspension system is available from Rubotherm (Bochum, Germany). The magnetic suspension separates the high pressure sample environment from the delicate balance. The system can operate up to 1000°C or 450 atm. The readers should note that the pressure and temperature limits cited throughout this article represent the manufacturers’ specifications, rather than any practical limits determined and recommended by the editor or the authors. Operation at reduced pressure is particularly valuable for determining the adsorption or absorption characteristics of materials. High pressure instruments may be used for studies of combustion, pyrolysis, catalysis, or nonstoichiometry.

Mass and Temperature Calibrations and Standards.

**Calibration of Mass.** Calibration of mass is conducted by weighing a standard mass (over 1 μg) at a controlled temperature. Room temperature is preferable, since buoyancy and aerodynamics add to the uncertainty when the

---

**Fig. 15.** Possible placements of the thermocouple relative to the sample in TGA (Gallagher, in Ref. 5).
experiment is conducted over a wide range of temperatures. Any changes due to these factors go into a blank or background correction.

For experiments over an extended period of time, such minor factors as fluctuations in room heating and air conditioning, exposure to sunlight, drafts, and other sources of temperature, and variable heat transfer from the furnace should be taken into consideration. These factors, along with vibration stability, should be considered when choosing a location for a TGA instrument. Generally, all TGA equipment gives precise data with only infrequent checks of the calibration with a standard mass. The starting mass for a TGA experiment is generally larger than that for DTA/DSC and is in the range of 6–10 mg for pure polymers and around 15 mg for filled or blended polymers.

For a simple calibration of weight loss, the weight loss of a standard material can be checked under reproducible conditions of sample mass, packing, heating rate, sample holder configuration and atmosphere type, flow, and pressure. The TGA of calcium oxalate monohydrate (CaC$_2$O$_4$·H$_2$O) is often used as a standard for the calibration of mass loss in thermogravimetry. This is due to three well-resolved steps in its thermal decomposition.

The three steps in Figure 17 are (1) the loss of H$_2$O to form anhydrous oxalate, (2) the loss of CO to form the carbonate, and (3) the loss of CO$_2$ to form CaO. The observed weight losses, determined from the integral curve (TGA), may be compared with the theoretical values obtained from the known stoichiometry
Fig. 17. TGA and DTGA curves for the thermal decomposition of calcium oxalate (CaC$_2$O$_4$, H$_2$O) in argon at 20°C/min (3).

of the process. Potential differences in the sample temperatures indicated by the TGA curve can arise when the starting masses differ significantly among the experiments. Plots of weight versus time should reveal the linearity of the heating rate in the range of the experiments. The derivative TGA curve (DTGA), shown in Figure 17, enhances resolution and gives a “fingerprint” of the decomposition process. DTGA curves always should accompany a TGA analysis. Such curves also are important for kinetic studies, since they are related to the actual rate of the reaction. Weight loss is, however, more readily evaluated from the integral curve. There is no international standard method for TGA, because all of the instrumental and experimental variables noted above cannot be fixed for different instruments and different laboratories. However, for a given instrument, standards for mass loss under carefully controlled conditions can be adopted for routine checks of reproducibility.

Temperature Calibration. As mentioned, temperature control and calibration of TGA equipment is more difficult. Not only are the sample and the thermocouple a finite distance apart, so as not to interfere with the weight measurement, but also the heat transfer between sample and oven in TGA is usually across an air or an inert gas gap. In addition, sample masses are often larger than those in DTA/DSC. There may be a large temperature gradient inside the sample. There are also other factors noted in the right-hand side of Table 5 that would affect temperature control.

Wunderlich (5) recommends that the actual sample temperature should be measured by using an external thermocouple in contact with the sample in the crucible and then running a heating scan. The thermocouple adds additional weight to the balance pan. Therefore, the mass information is lost. Two methods commonly used to measure sample temperature in relation to the sensor temperature are (1) magnetic standards and (2) “fusible links.” They have been found to work equally well in a comparison study (42).
In the “fusible link” method a small weight hangs at the end of a metal link. The link takes the normal position of the sample. When the link melts, there is a sharp break in the TGA curve. The temperature at the break point is the $T_m$ of the metal, which should be known beforehand. The second method uses the Curie temperature ($T_c$) of a ferromagnetic material. A pellet of the reference material is placed in the field of a magnet, placed outside the balance. Because of the effect of the magnet, the actual weight measured by the thermobalance is either less or more than the true weight. As the Curie temperature of the standard material is reached, the magnetic effect vanishes and an equivalent increase or decrease of weight is recorded. A nice feature of using magnetic materials is that there is no interaction between different samples and multimetal sandwiches of magnetic standards can be used in a single experiment to obtain several calibration points. Representative curves for a series of magnetic standards are shown in Figure 18 (43). The heating and flow rates used for calibration should be the same as those chosen for subsequent experiments.

A series of magnetic reference metals are available from NIST. Gallagher (5) lists the selected metals and alloys for potential use as magnetic standards. The ICTAC Committee for Standardization has conducted an extensive round-robin study to establish the calibration procedures and recommended temperatures for various standards (44). An inert gas ($N_2$, Ar) whose thermal conductivity...
approximates that of the gas to be used in subsequent experiments should be used instead of oxygen, since these metals are liable to be oxidized. An ASTM method describes the practice for evaluating the temperature scale for thermogravimetry (ASTM E914). A recent proposal (Ref. 5, p. 48) is to use the ignition temperature of selected organometallic compounds for temperature calibration. There is an abrupt weight loss at the ignition temperature of these compounds. The temperature of ignition can be previously calibrated using DSC or DTA, which again has been calibrated using metallic standards to conform to the International Temperature Scale. ICTAC recommendations should be followed in reporting TGA data.

The present trend in thermal analysis is toward smaller samples and furnaces, as well as faster heating and cooling rates in order to obtain minimum turnaround times. As these trends continue, temperature calibration will remain a major consideration and probably increase in importance. For recommendations on the presentation of data, the reader should consult ICTA recommendations (2).

**Application of TGA/DTGA in Polymers**

The principal applications of TGA/DTGA in polymers are (1) determination of the thermal stability of polymers, (2) compositional analysis, and (3) identification of polymers from their decomposition pattern. Also, TGA curves are used to determine the kinetics of thermal decomposition of polymers and the kinetics of cure where weight loss accompanies the cure reaction (e.g., as in condensation polymerizations, such as cure of phenolic resins). The latter will not be discussed here.

**Thermal Stability of Polymers.** Thermogravimetry has become a general method for comparing the thermal stability of polymers. In comparing thermal stability, it should be remembered that TGA measurements only record the loss of volatile fragments of polymers, caused by decomposition. TGA/DTGA cannot detect any chemical changes or degradation of properties caused by crosslinking. Examples of Degradation (qv) involving cross-linking without weight loss are the degradation of styrene-co-butadiene rubber (SBR) and butadiene rubber (BR) or their blends, although at high temperature they decompose into fragments with loss of weight that can be detected by TGA/DTGA. Small sample sizes and low heating rates prevent any dramatic influence of reaction heat that accumulates at high heating rates. However, there are some exceptions when small sample size and low heating rate do not yield satisfactory results.

A strict comparison of thermal stability can only be made when the samples are evaluated under identical conditions. Figure 19 shows an example of the stability determination of poly(vinyl chloride) (PVC) and polystyrene (PS) and a 50:50 blend of the two polymers by weight (45). The two inside curves are for (1) the predicted behavior for the blend, based on the neat PVC and PS curves, and (2) the actual experimental curve for the blend. Under thermal decomposition conditions, there is some possibility that any of the components or their degradation products can interact with one another causing either (1) greater stability for the blend, (2) less stability for the blend, or (3) no change in stability. The case of PVC and PS seems to be one where the blend is more stable than the individual
pure polymers (Fig. 19). The shift of curve 2 to higher temperatures as compared to curve 1 indicates that some interaction between the components is taking place leading to mutual stabilization. This may be due to reducing the kinetic chain length (and rate) for dehydrohalogenation of HCl in the PVC component. It will also be dependent on the degree of mixing of PVC and PS in the blend. Examples of polymer blends that are less stable than the pure polymers, to name a few, are PVC/PMMA poly(methyl methacrylate) and (PVC)/PVA poly(vinyl acetate). PS and PMMA blends show no evidence of interaction; thus the thermal stability of their blends neither increases nor decreases.

**Compositional Analysis of TGA/DTGA.**

**Copolymers.** If different segments of the copolymer chain have different thermal stabilities, it is possible to quantitatively analyze certain polymers by TGA. The classical example is the polyethylene-co-(vinyl acetate) polymer or EVA. When EVA is thermally degraded in an inert atmosphere, the first product emitted at about 350°C is acetic acid. The rest of the hydrocarbon chain decomposes at a higher temperature (430°C). This is shown in Figure 20 (Ref. 5, p. 870). The weight loss at 350°C corresponds to the amount of vinyl acetate present in the copolymer.

The amount of vinyl acetate can be calculated from the weight loss as follows:

\[
%\text{vinyl acetate} = \%\text{weight loss} \times 1.43
\]  

**Rubber Vulcanizes.** One of the common uses of TGA/DTGA analysis in the rubber industry is to determine the composition of a rubber formulation, either cured or uncured. The general TGA/DTGA procedure for elastomer
Fig. 20. Weight loss curves of several ethylene/vinyl acetate copolymers. The ethylene/vinyl acetate composition is shown next to each curve. The heating rate was 10°C/min (Hale and Bair, in Ref. 5).

Vulcanizate analysis is illustrated in Figure 21 (46). The standard test method for compositional analysis by TGA (47) provides a method for determining four arbitrarily defined components: (1) highly volatile matter, (2) matter of medium volatility, (3) combustible material, and (4) ash, left after oxidative decomposition of inorganic components. The materials fitting this description in the case

Fig. 21. Schematic TGA and DTGA curve for compositional analysis of a rubber vulcanizate (46).
of elastomer vulcanizates are depicted in Figure 21 and described in Table 6. The definition of each component is based on its relative volatility. The success of the method depends on each component having a different thermal stability range in an inert atmosphere and in an oxidizing atmosphere. The standard method for compositional analysis by thermogravimetry is described in ASTM E1131.

The analysis is performed by first taring the microbalance and then introducing the sample. The initial weight is set after establishing an inert atmosphere. Next the desired heating program is started and the specimen weight continuously monitored in the recorder. The ordinate setting can be either weight in milligrams or percentage of the original sample weight. As noted in Table 6, the first weight loss (~150–350°C) is due to highly volatile matter. For a vulcanized rubber, this generally consists of the amount of oil added as a processing agent and a small amount (~1–2%) of decomposed fragments of the vulcanizing agent (sulfur peroxide), vulcanization accelerators and antioxidants, emulsifiers, etc. Moisture, if present, evolves at a lower temperature. The second fraction (~350–550 or 600°C) represents the amount of polymer decomposed. After the plateau of the second or “medium volatile matter” weight loss has been established (~600°C), the atmosphere is changed from inert to oxidative.

In the case of an elastomer vulcanizate that contains Carbon Black (qv), the sample is first cooled to ~300 to 400°C before changing to air or oxygen. This is to ensure that the initial oxidation atmosphere is at a lower temperature than the carbon black oxidation temperature. The modified procedure often permits the identification of carbon blacks from the weight-loss profile (48). The combustible material refers to oxidizable material (eg, carbon black, graphite), which is not volatile in an inert atmosphere at temperatures up to 750°C. In the absence of nonblack fillers, the ash is mostly composed of zinc oxide, which is a component in

| Table 6. Definitions of Different Fractions in Thermogravimetric Analysis of Elastomers*
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Highly volatile matter</td>
<td>Refers to moisture, polymer, diluent, oil, plasticizer, emulsifiers (eg, in styrene–butadiene rubbers), curatives (sulfur, accelerator), antioxidants, antiozonants, and other low boiling components (approx. 300°C or lower)</td>
</tr>
<tr>
<td>Medium volatile matter</td>
<td>Refers to medium volatility material such as processing oil, processing aid, elastomer, resin (used as curing agent), etc. In general, these materials degrade at 300 to 750°C.</td>
</tr>
<tr>
<td>Combustible material</td>
<td>Refers to oxidizable material, not volatile (in the unoxidized form) at 750°C or some stipulated temperature dependent on the material (eg, carbon black, graphite, etc).</td>
</tr>
<tr>
<td>Ash</td>
<td>Refers to nonvolatile residues in an oxidizing atmosphere which may include metallic oxides, filler or inert reinforcing material (eg silica). In the absence of nonblack fillers, the ash is composed of zinc oxide which is a component in most vulcanizates. A small amount of ash (&lt;1%) may be due to elastomer residue.</td>
</tr>
</tbody>
</table>

*From Ref. 47.
most vulcanization recopies. The analysis is complete when a weight-loss plateau, corresponding to the residual sample mass, is established. Several reviewers have stressed the use of smaller sample sizes (for better resolution, lower heating rate) and an inert atmosphere of high thermal conductivity (eg, helium). In using small samples it may be useful to characterize multiples to ensure that the results are representative of bulk material. The residue may be analyzed to determine the nature and amount of inorganic components by using X-ray fluorescence.

Factors that influence the accuracy of the component analysis procedure are the following. The above discussion assumes that there is no high boiling oil present as a processing aid that can interfere with detecting clearly the initial breakdown point of the polymer and no mineral filler (which may have water of crystallization or other constituents that escape around the temperature of the “highly volatile matter”). Also, it is important to note that the determination of carbon black by the suggested method is accurate only for hydrocarbon elastomers, which degrade cleanly in an inert atmosphere at temperatures below 500°C. Elastomers with a heteroatom in the molecule leave a char residue, which volatilizes along with carbon black during the oxidation stage. Resin curing agents also will interfere with polymer determination. Graphite, if present, can be determined by oxidation at a higher temperature (∼800°C). These and numerous other considerations, as well as possible remedies, have been discussed in considerable detail by Sircar (49).

Despite the above-cited difficulties, TGA-DTGA analysis remains a useful tool for the compositional analysis of rubber vulcanizates. It is a straightforward, reasonably accurate process and is much faster than classical extraction methods. Also, it is an excellent quality control tool for determining possible weighing errors and reproducibility for elastomer batches in a production setting. Thus, TGA-DTGA is the method of choice for compositional determinations for cured and uncured elastomer compounds, as well as for many other polymer compositions.

Identification of Elastomers. Sircar and co-workers (Ref. 5, p. 1278) developed a unique and very useful DSC and TGA/DTGA protocol for identifying elastomers. It involves using the measurement of \( T_g \) and the degradation patterns for many elastomers and their blends in both nitrogen and oxygen. On the basis of this, they classified elastomers into three principal groups according to their degradation characteristics in nitrogen: (1) those exhibiting an endotherm (eg, polyethylene, EPDM, butyl rubber); (2) those exhibiting an exotherm (eg, SBR, BR, NBR); and (3) those exhibiting multiple peaks, both exotherm and endotherm (eg, NR, IR). For details on using the protocol, the reader is referred to the above reference.

Controlled Rate Thermogravimetry. Gallagher (5) describes controlled rate thermal analysis. In the case of mass loss, the rate of change of temperature is controlled by a preset rate of weight loss or change in partial pressure. Gallagher describes three different modes of controlled rate TGA and also dynamic TGA with isothermal rest periods. In the first mode, the operator chooses a fixed rate of weight loss (eg, X%/min) and the temperature programmer maintains that rate of change, sometimes by both heating and cooling at different times. The second mode is similar to the first mode, except that the sample is always
Fig. 22. Weight loss curves for a 72:28 ethylene/vinyl acetate copolymer. Curve A was obtained at 10°C/min rate of heating. Curve B was obtained using Autostepwise software, which automatically slows down the heating rate when a sharp change in weight loss is detected, and increases the rate when little change in weight loss is observed (from Hale and Bair, in Ref. 5).

dynamically heated. TA Instruments, Inc. (50) markets a commercial software package called “Hi-Res TGA.” It operates so that the heating rate approaches a preset maximum during periods of no mass loss. As the mass change is sensed, however, the heating rate automatically slows depending upon two parameters set by the operator (resolution and sensitivity). The aim is to improve resolution while minimizing the total time for the experiment. The third controlled rate option is called stepwise (or autostepwise) isothermal measurement and involves one or more isothermal steps as the weight loss reaches a threshold level. The necessary software and instrumentation are available through Seiko Instruments (currently marketed by Mettler-Toledo) (51).

An example of autostepwise TGA shows an improvement in resolution for weight-loss curves of EVA samples. Without the autostepwise rate control it is evident (Fig. 20) that the end point for the acetic acid evolution is not distinct. The acetic acid weight loss curves are not completely level before the residual polymer fraction starts decomposing. As shown in Figure 22, the resolution can be much improved by using the High-Res or autostepwise TGA technique enabling more quantitative information. The figure shows an initial weight loss of 18.4%, corresponding to a vinyl acetate content of 26.3% versus the known value (supplied by the manufacturer) of 28%.

Simultaneous or Combined Techniques. Many of the simultaneous or combined techniques that include TGA as a component have been described while discussing DSC/DTA techniques. Others with TGA as a component are TGA-EGA or EGD, TGA-MS, TGA-FTIR, TGA-GC-MS, TGA-MS-MS, and TGA-APCI-MS. APCI stands for atmospheric pressure chemical ionization. More details are available in the reference by Gallagher (5). The other acronyms, not mentioned in Table 1, are as follows: mass spectrometry (MS), Fourier transform infrared spectrometry (FTIR).
Thermomechanical Analysis

Thermomechanical analysis (TMA) measures the deformation of a material contacted by a mechanical probe, as a function of a controlled temperature program, or time at constant temperature. TMA experiments are generally conducted under static loading with a variety of probe configurations in expansion, compression, penetration, tension, or flexure. In addition, various attachments are available to allow the instrument to operate in special modes, such as stress relaxation, creep, tensile loading of films and fibers, flexural loading, parallel-plate rheometry, and volume dilatometry. The type of probe used determines the mode of operation of the instrument, the manner in which stress is applied to the sample, and the amount of that stress.

**TMA Instrumentation.** For accurate measurements of the change in dimension of small samples, the device generally used by most manufacturers of TMA is called a linear voltage differential transformer (LVDT). This device, as configured in a Perkin-Elmer TMA module, is shown in Figure 23. For distinguishing between expansion and contraction, the sign of the output voltage changes with the direction of motion. The device can readily detect changes of the order of 0.1 μm. Testing for linearity of the range of output voltage of an LVDT (mV/μm) is frequently performed by measuring gauge blocks of a sheet metal. For accurate work, it is necessary to provide compensation for the dependence of the output on temperature. The instrument shown in Figure 23 is typical of a single rod module, based on LVDT. Contemporary TMA instruments use closed
loop electromagnetic circuits to accomplish constant loading and positioning of the probe as compared to older instruments where mechanical placement of the weights was used. The instrument in Figure 23 is reported to be capable of detecting changes as small as 3 nm and can operate in the temperature range −170 to 1000°C. The resolution is around 0.1 μm, when the instrument is operated carefully over a range of temperatures. Temperature-sensitive components such as the LVDT generally are isolated from the high temperature environment of the sample.

Optical instruments that use laser interferometry have much greater sensitivity with an accuracy of 0.02 μm or 1/32nd of the laser wavelength used. The surfaces for the sample and the reference specimens need to be polished for this kind of accuracy. Also, the high temperature limit is governed by the loss of reflection from the mirrored surfaces and is around 700°C, as compared to a maximum of 2000°C for the LVDT-based instruments.

For determining the coefficient of linear expansion, it is a common practice to generate $\Delta L/L_0$ curves with and without the sample. The two curves are subsequently subtracted to compensate for the expansion of the sample holder. For convenience, it is best to use a standard reference material, eg, an isotropic metal such as aluminum or platinum (52), as the sample holder. In Figure 24, we see that, compared to other isotropic materials, quartz (fused silica) has a very low thermal expansion coefficient ($6 \times 10^{-6}/°C$). It is also easily formed. If the upper temperature limit (<1100°C) is acceptable, then use of a quartz sample holder may permit ignoring the small correction for the linear thermal expansion of the sample holder, with very little effect on accuracy. If the upper temperature limit is over 1100°C, a high temperature material such as alumina or platinum is the material of choice and the correction is substantial. Another way to reduce the correction is to use the instrument in a differential fashion. Both the
optical and the LVDT instruments can be used in this fashion with the reference (a standard material) pushrod connected to the coil and the sample rod to the core. To obtain the correction accurately, the sample and the reference should have the same length. It is also necessary to maintain thermal equilibrium by keeping the heating and cooling rate low. This also avoids a thermal gradient inside the larger-sized samples typically used for TMA. It is necessary to allow sufficient time to equilibrate if programming several isothermal steps is the temperature profile followed.

A temperature calibration procedure for TMA has been proposed (53–55) and subsequently included as an ASTM method (Test Method for Temperature Calibration of Thermomechanical Analyzers, E1363-90). It uses a penetration probe and the melting temperature of one or more standard materials. Pure metals with sharp melting points are the standards often used. An open DSC pan may be used to contain the calibrant material. Another potential material would be the selected shape memory alloy, reported to be reproducible to ±1°C (56). Several reviews on temperature calibration for TMA have been published based on ASTM efforts in this area (54,55). Sircar (26) suggests that, when used for elastomer evaluation, temperature calibration for TMA should be conducted with low melting liquids as in DSC. For calibration of the expansion, one manufacturer’s manual (TA Instruments) recommends aluminum for calibrating the linear expansion parameter. Other calibration standards suggested for the linear coefficient of thermal expansion (CTE) are lead (57) and copper (58).

Sample Preparation and Procedure. Sample preparation for CTE measurement is somewhat more rigorous for TMA than for either DSC or TGA. Samples with flat parallel faces (∼7 mm² × 1 to 2.5 mm in thickness) may be used. The larger the sample thickness, the greater will be the possibility of thermal gradients developing within the sample. ASTM D696 describes a recommended procedure for determining the coefficient of linear expansion of plastics. A general test method for solids (Test Method for Linear Expansion of Solid Materials by Thermomechanical Analysis, E831-86) is also available. Not all polymers and, particularly some elastomers, are amenable to TMA study. For example, a flat surface, to allow intimate contact of the sample and the probe, cannot be cut from a gum elastomer of high molecular weight. Maurer (59) has recommended hot pressing, which works for lower molecular weight gum rubbers. Silica powder also has been used to level the surface of gum elastomers (60). For penetration measurements the surface does not need to be smooth.

For Thermosets (qv), a flat surface can be achieved by molding, machining, or melt-pressing the sample. If the sample is punched, the burred edges must be removed or the sample placed burred edge up. Prime (Ref. 5, p. 1447) advises that the sample be conditioned in the TMA apparatus by heating to just above \( T_g \) and cooling with the loaded probe in place. This helps in relieving the internal stress, removes thermal history (e.g., the effects of physical aging), and allows the sample to conform to the probe. For samples that are not fully cured, care must be taken not to advance the degree of cure while following this procedure.

For \( T_g \) studies in elastomers, the ASTM E831-86 procedure must to be modified (26). After the probe is zeroed at room temperature, the sample is placed on the TMA platform and cooled to \(-120^\circ C\) under liquid nitrogen purge at 50 mL/min. After equilibration at \(-120^\circ C\) for 10 min, a 0.5–1-g weight (10 mN) or
equivalent force is placed on the top of the pan. This places the probe in contact with the hardened elastomer sample. The thickness of the sample is measured and the probe zeroed. The sample is ramped at a low rate of heating (2–5°C/min) under 50 mL/min of nitrogen purge from −120°C to 100°C. For presentation of data, the ICTAC recommendations (2) are followed.

The above procedure differs from ASTM E831 in two important ways. First, the weight should be added only after the elastomer sample is rigid (below \( T_g \)) to avoid compression; and second, a small weight of only around 0.5 g or less is necessary to ensure intimate contact. Larger weights (1–3 g, as recommended for plastics by ASTM E831) may again compress the elastomer as it reaches temperatures above \( T_g \). A static weight of 10 g or more or the equivalent force is generally used with a penetration probe.

**Probe Configuration for TMA.** Typical probe configurations for TMA have been described by Maurer (59) and Earnest (25). Figures 25a to 25e are from Earnest (25), whereas 25f and 25g are from Wendlandt (4). The coefficient of linear expansion uses a probe of greater surface area and is operated under negligible load (Fig. 25a). A high loading converts it to a compression probe for elastomeric materials and the results differ with load. Figures 25b, 25c, and 25f show various penetration probes. The hemispherical probe can also be used as an expansion probe. Ennis and Williams (61) used the hemispherical probe to determine linear expansion of thermosets and claim better accommodation of probe misalignment with this type of probe. Figures 25d and 25e are for tensile and flexure modes, respectively. For anisotropic materials, the determination of linear expansion does not give the volume expansion by a simple calculation. However,
TMA also can be used to determine volume expansion by using a fluid to surround the sample in a cylinder and piston arrangement, as shown in Figure 25g. This is similar to a dilatometer. Another method uses a vitreous silica dilatometer (ASTM E228). Special instrumentation has been designed to determine the coefficient of thermal expansion of fibers using TMA (Ref. 5, p. 1974). For “fingerprinting” of fibers, TMA offers more detail than either DSC or DTA. Therefore, TMA is the preferred technique if the study is limited to only a single method.
**Derivative TMA.** An example illustrating the use of different probe configurations for determining linear expansion in both the glassy and the rubbery states, as well as $T_g$ of chloroprene rubber (neoprene, CR) (62), is presented in Figure 26. Note the use of the derivative signal (DTMA) for both the loaded expansion (penetration) and tension measurements. The derivative plot aids in locating the transitions or relaxations, which are not prominent, and also defines a reproducible transition point in cases where a diffuse transition is encountered. DTMA of tension measurements is a sensitive technique for evaluating polymer blends. Several transitions are reproducibly detected by this method when other modes may fail. The $T_{go}$ values are the glass-transition temperatures reported in the literature. They correspond to the inflection point of the DSC curves ($T_{eo}$) in Figure 7. $T_{gd}$ is slightly different and corresponds to the peak of the derivative DSC curve (see $T_p$ in Figs. 7 and 8). Sircar (26) determined $T_g$ values for eight elastomers using TMA (expansion and penetration probes), DSC, and DMA. He found that $T_g$(expansion) and $T_g$(penetration) have somewhat different values and the latter is closer to that determined by DSC. The differences in the $T_g$ values are due to the differences in the temperature dependence of the different thermal properties being measured by different techniques: specific heat capacity in the case of DSC, linear expansion with the TMA expansion probe, and modulus in the case of the TMA penetration probe.
Illustrative Examples for TMA.

Expansion Mode. Figure 27 (64) illustrates the calculation of the CTE from the slope of the TMA curve of an epoxy printed circuit board and the use of the derivative (DTMA) to directly record the coefficient of linear expansion (α). Thermosetting polymers, especially when highly filled, can absorb moisture from the atmosphere. Moisture acts as a plasticizer and has the effect increasing α and lowering T_g. The process is reversible. While moisture in polar polymers is often tightly bound, desorption may occur on heating during the measurement. This will be discussed at greater length below. In this case the measurement will reflect the sum of thermal expansion and hygroscopic contraction. Purely thermal expansion then can be measured in a second run after the sample has been thoroughly dried.

Penetration Mode. TMA in the penetration mode can be used to evaluate the degree of cure of thermoset materials (64). A large load (typically, 10–100 g or 0.1–1.0 N) is employed for these experiments. The probe measures the softening associated with the large decrease in modulus as the temperature approaches T_g. The softening point correlates well with T_g (65,66). The penetration probe referred to in Figure 28 is a small-radius (0.48 mm) hemispherical probe. The smaller amount of penetration for sample A indicates that this is more highly cross-linked of the two samples.

Flexure Mode. Figure 29 illustrates TMA data for a two-layer insulation wire coating. Using the knife-edged three-point bend flexure probe (67) accentuates the softening that occurs at the glass-transition temperature. It is remarkable that the softening of both the outer layer of polyester and the inner layer of poly(amide–imide) were easily detected.
**Degree of Cure.** As shown in Figure 27, the $T_g$ is taken as the extrapolated intersection for the glassy and rubbery state curves. Typically, thermal expansion in the rubbery state is about three times that in the glassy state. The $T_g$ determined by TMA (using either an expansion or penetration probe), is often related to the degree of cure for thermosetting polymers, as was mentioned in the discussion of DSC and illustrated in Figure 9. As the degree of cure increases, $T_g$ increases and the coefficient of linear expansion ($\alpha$) decreases. Thus, a relationship between $T_g$ and conversion, independent of the temperature of cure, exists for most thermosetting systems. This will be discussed further later in this presentation. Also, a direct proportionality exists between the deflection temperature under load (ASTM D648) and the TMA $T_g$ determined in either the expansion or the penetration mode. Sykes and co-workers (68) describe a fixture to measure a TMA heat distortion temperature (HDT) as defined in ASTM D648. For printed circuit board materials, Lamoureux (66) observed a correlation between $T_g$ by TMA expansion and softening temperature determined by TMA penetration (as described above by Sykes and co-workers). For an elastomer compound, Brazier and Nickel (63) found a correlation between $T_g$, determined by TMA (expansion and penetration mode) and Gehman rigidity temperature.

Unlike thermosetting materials, the $T_g$ of elastomers does not increase significantly with the degree of cure. However, the penetration temperature under a fixed load will increase with cure and can be used as a measure of the degree of cure of an elastomer compound. This is illustrated in Figure 30 (69) and is based on the fact that the elastomer modulus increases with cure.

*Fig. 29.* Use of the TMA knife-edged flexure probe to determine the softening point of both the outer and inner coatings of a motor-winding wire (67).
Dynamic Mechanical and Dielectric Analysis

Dynamic mechanical (DMA) and dielectric analysis (DEA) methods are used both to study molecular relaxation processes in polymers and to determine inherent mechanical and dielectric properties. DMA measurements involve mechanical excitation by imposing a small cyclic deformation to a sample and measuring the stress response. DEA involves imposing a cyclic (or alternating) electric field to a sample and observing the electric polarization or current induced in the sample.

DMA methods are widely used by thermal analysts to determine the viscoelastic properties of polymers for a number of purposes. The primary application of these techniques to the study of polymeric solids and melts is well documented. Excellent general discussions covering the subject are provided in References 70–72. Linear amorphous polymers exist in a number of characteristic physical states depending on the time scale and temperature of measurement. These are illustrated in Figure 31 in terms of an arbitrary modulus function and are classified as glassy, leathery, rubbery, rubbery flow, and viscous (73). All linear amorphous polymers exhibit these five physical states when they are observed over a wide range of time or temperature. Polymers that are either cross-linked or crystalline do not exhibit the rubbery flow and viscous responses as illustrated.

Region 2 in Figure 31 corresponds to the glass transition, which serves as an important benchmark or corresponding state for viscoelastic response. The particular physical state that the polymer exhibits during a DMA measurement reflects the extent to which the rate of molecular motion or relaxation compares to the test rate at a given temperature. In general, the modulus decreases either with decreasing test rate or increasing temperature. In fact, there is a strong relationship between time and temperature.
In most commercial dynamic mechanical instruments a steady-state alternating strain is applied such that

$$\varepsilon (u) = \varepsilon_0 e^{iu\omega}$$

is the generalized sinusoidal strain function in complex notation, where $\varepsilon_0$ is the strain amplitude, $\omega$ is the radian angular frequency of the sine wave (rad/s), and $u$ is the historical time, $u \leq t$ ($u = 0$ at $t = 0$). An analysis of the cyclic stress and strain provides that the steady-state ratio of stress to strain is (70,73) a complex quantity having both in-phase and out-of-phase components.

$$\sigma (t) = E^* \frac{E'}{E''} = E' + iE''$$

Here $\sigma(t)$ is the stress at time $t$ and $\varepsilon$ is the strain; $E^*$ is the complex dynamic mechanical modulus, $E'$ is the ratio of in-phase stress to the applied strain, and $E''$ is the ratio of out-of-phase stress to strain. The out-of-phase stress leads the strain by $90^\circ$. Further, it can be shown that $E'$ is related to the mechanical energy stored per cycle and $E''$ is related to the energy converted to heat through viscous dissipation. As a result, $E'$ is referred to as the storage modulus and $E''$ is called

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**Fig. 31.** Diagram of master curves for modulus and loss tangent for a typical amorphous polymer showing five characteristic physical states (73).
Fig. 32. Simple relationship between stress ($\sigma$) and strain ($\varepsilon$) in dynamic mechanical tests illustrating the role of the phase angle, showing (a) Hookian elastic response, (b) viscoelastic response, and (c) vectorial representations of complex oscillatory stress/strain response (74).

the loss modulus. The material loss factor or loss tangent is

$$\tan \delta = \frac{E''}{E'}$$

representing the ratio of energy dissipated to energy stored per cycle of deformation. In a physical sense the storage modulus is related to the stiffness of the material and the loss modulus is reflected in the damping capacity of the material.

On the basis of the complex representation for the dynamic mechanical modulus, the relationships between stress and strain can be considered on a complex plane in terms of vectors (74), as shown in Figure 32c. The applied strain of magnitude $\varepsilon_0$ is out of phase with the resulting stress of magnitude $\sigma_0$ by an amount represented by angle $\delta$. The stress components of $\sigma^*$ are resolved as $\sigma'$, in-phase, and $\sigma''$, 90° out-of-phase with $\varepsilon^* = \varepsilon_0$.

Further, Figure 32b illustrates that the phase shift between the cyclic stress and strain for a viscoelastic material results in a hysteresis loop, the size of which reflects the rate of viscous dissipation or heat generation during the cyclic deformation. For an ideal Hookean material, there is a zero-area loop (Fig. 32a). But as $\tan \delta$ increases, so does the size of the hysteresis loop. This notion is particularly important in applications such as the damping of vibration and sound.

DMA experiments are performed under conditions of very small strain so that the material response is in the “linear viscoelastic” range. This means that the magnitude of stress and strain are linearly related and the deformation behavior is completely described by the complex modulus function, which is a function of time only. The theory applies both for the case of a tensile deformation or simple extension and for shear. In the latter case the comparable modulus is $G^*(\omega)$, with components $G'(\omega)$ and $G''(\omega)$. As a first-order approximation, $E = 3G$. The theory is developed assuming deformation under isothermal conditions, and temperature does not appear (nor is implicit) as a variable.
Dielectric analysis (DEA) measures changes in the properties of a polymer as it is subjected to a periodic (or alternating) electric field. In DEA a sample is placed between two electrodes. The traditional electrode geometry used for thermoplastics is a parallel-plate capacitor. The parallel-plate electrode measures the bulk dielectric response of the material subjected to a sinusoidal voltage applied to the electrodes. The electrodes typically are formed by vapor deposition or sputtering of a metal onto the polymer surfaces. A more contemporary dielectric electrode geometry is the interdigitated comb type of electrode which is particularly well suited for in situ process monitoring. This will be discussed in more detail in a later section.

In DEA the applied voltage establishes an electric field in the sample. In response to this field, the sample becomes electrically polarized and conducts a net charge from one electrode to the other. This gives rise to a current whose amplitude is dependent on the frequency of the measurement as well as the temperature and structural properties of the polymer (or dielectric) being tested. The measured current is at the same frequency as that of the field (voltage) but shifted in phase and amplitude. The phase angle $\delta$ and the relative difference in amplitude between current and voltage provide data on dielectric properties.

In the following discussion it should be noted that we use the same symbol, $\varepsilon$, to represent both mechanical strain and the electrical dielectric constant. This is based on common terminology from the literature and should not cause the reader any difficulty, since both are used in differing contexts. $\varepsilon^*$ represents the complex dielectric constant, $\varepsilon'$ the in-phase component or permittivity, and $\varepsilon''$ the out-of-phase component or dielectric loss factor. It is also important to note that the dielectric “constant” is not a constant but is strongly dependent on both frequency and temperature.

A dielectric experiment is analogous to a DMA experiment where the charge is mathematically comparable to the strain and the voltage is comparable to the stress. The mathematical analysis is similar and, assuming a single relaxation time model for simplicity, it can be shown that the complex dielectric constant $\varepsilon^*$ has the form $\varepsilon^* = \varepsilon' - i \varepsilon''$ with

$$\varepsilon' = \left[ \varepsilon_u + \frac{(\varepsilon_r - \varepsilon_u)}{1 + (\omega \tau)^2} \right] \times E'_p$$

$$\varepsilon'' = \left[ \frac{\sigma}{\omega \varepsilon_0} + \frac{(\varepsilon_r - \varepsilon_u)\omega \tau}{1 + (\omega \tau)^2} \right] \times E''_p$$

Here $\sigma$ is the bulk ionic or dc conductivity; $\omega$ is the angular frequency ($2\pi f$); $\tau$ is the dipole relaxation time; $\varepsilon_r$ is the relaxed dielectric constant or low frequency/high temperature dielectric constant (relative permittivity due to induced plus static dipoles); $\varepsilon_u$ is the unrelaxed dielectric constant or high frequency/low temperature dielectric constant (relative permittivity due to induced dipoles only); $\varepsilon_0$ is the permittivity of free space; $E'_p$ is the electrode polarization term for permittivity; and $E''_p$ is the electrode polarization term for loss factor. The value of $E'_p$ and $E''_p$ is usually unity, except when ionic conduction is very high (75).
Many polymeric materials consist of dipoles (chemical bonds which have an unbalanced distribution of charge in a molecule) and traces of ionic impurities. If a polymer containing polar groups is heated so that an immobile dipole becomes mobile, an increase in permittivity is observed as the dipole starts to oscillate in the alternating electric field. This effect is referred to as a dipole transition and has a characteristic relaxation time ($\tau$) associated with it (76). When exposed to an electric field, the dipoles tend to orient parallel to the field direction and the ions move toward the electrodes, where they form layers. The dipole relaxation time is the time required for the dipoles to fully align, and the cycle time (reciprocal of frequency) is the time required for the electric field to change polarity.

The permittivity is a measure of the alignment of the dipoles in the applied electric field, while the loss factor represents the energy required to align the dipoles and to move the free ionic impurities. Both of these dielectric parameters depend on the temperature and the structure or composition of the material. The loss tangent

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$

relates to the phase shift between the current, $I(t)$, and voltage $V(t)$, which results from the lag in dipole response with respect to the applied field, as indicated in Figure 33. Tan $\delta$ is often referred to as the dissipation factor. The functional forms of $\varepsilon'$, $\varepsilon''$, and tan $\delta$ are shown in Figure 34, which represents the mathematical relationships for the dielectric functions calculated for a simple single relaxation model (71).

Most organic materials have permittivities ranging from 2 to 10. Polymers at temperatures well below the $T_g$ generally have loss factors less than 0.1. When heated to $T_g$ and above, they can have loss factors as high as $10^4$ (71). Because of its large variation with the physical state of a material, the loss factor is a most useful function for the cure monitoring of thermosets.

Dielectric analysis is used most frequently with thermoplastics to provide information on and an understanding of the molecular basis for relaxations. This is a more traditional context for DEA and ample information with numerous
interesting examples is available in the literature, particularly in the text by McCrum (71) and the review by Chartoff (77). The reader is referred to these references for further insights. More recently, DEA has had extensive applications in the characterization and in situ process monitoring of the cure of thermosets, particularly in the manufacturing of composites. Since this topic is not as well known, we summarize in a subsequent section some of the more salient aspects of the use of DEA for the cure characterization of thermosets.

Applications of DMA in Characterization of Thermoplastics

Determining $T_g$ by Dynamic Mechanical Analysis. Dynamic mechanical methods are popular among thermal analysts for measuring thermomechanical properties. Identifying the glass transition and how various system modifications affect $T_g$ is a major application for DMA. Generally, the glass transition is easily identified from dynamic mechanical data because of the sharp decrease in storage modulus $E'$ (or shear storage modulus $G'$), and the
corresponding loss dispersion in $E''$ (shear loss $G''$) or $\tan \delta$ that occur at $T_g$, as shown in Figure 35. These data are for a typical amorphous polymer (78). It is evident that there is latitude in how the exact value of $T_g$ is chosen from a set of dynamic data, and this often leads to confusion in the literature. The criterion for selection of $T_g$ from DMA data is usually either the peak in loss modulus $E''$ or peak $\tan \delta$. While the peak $\tan \delta$ is often used in the literature, the $T_g$ value obtained is several degrees higher than peak $E''$. The $\tan \delta$ peak corresponds more closely to the transition midpoint of the decreasing log $E'$ curve, while the loss modulus peak more closely denotes the initial drop from the glassy state into the transition. In this respect the $E''$ peak $T_g$ value is generally close to the intersection of the two tangents to the log storage modulus curve originating from both the glassy region and the transition region, the so-called “onset” temperature.

In general, the maximum loss modulus is the most appropriate value. This is the method prescribed by ASTM D4065. It is a reasonable criterion from a practical point of view because the upper use temperature of many amorphous polymers is the “softening” point. It is clear that by the transition midpoint (peak $\tan \delta$) the softening point has been exceeded.
For most linear amorphous polymers the transition region is rather narrow, covering around 15°C. In these cases the distinction between peak $E''$ and $\tan \delta$ is not substantial. There are cases such as in crystalline polymers or cross-linked thermosets where the $T_g$ region is broad and neither peak $E''$ or $\tan \delta$ may be appropriate. Also in the case of both highly crystalline polymers and cross-linked polymers, $T_g$ is a less prominent event and may be difficult to observe because the loss dispersion is not distinct. This is illustrated in Figure 36 (79). These data will be discussed further in a subsequent section. However, in general, the glass transition in crystalline and cross-linked polymers may be observed more clearly in DMA than by DSC, because the base line deflection ($\Delta E'$) at $T_g$ is much larger than the $\Delta C_p$ measured in DSC. The change in modulus at $T_g$ is often of the order of 10 to $10^3$, while the $\Delta C_p$ change will be of the order of 10–30%.

**Viscoelastic Relaxation Processes.** There are several relaxation processes that are observed in polymers at temperatures below $T_g$. These relaxations, in addition to the major glass–rubber relaxation, are of continuing scientific interest and engineering importance. They are intimately associated with the stiffness of engineering thermoplastics, impact toughness, diffusion rates of low molecular weight vapors and liquids, and the effectiveness of plasticization, among others. A more detailed review of these is presented by Chartoff (77).

For isochronal (constant frequency) experiments on Semicrystalline Polymers (qv) in the temperature range between the crystalline melting point and liquid nitrogen temperature (−196°C or 77 K), at least three relaxation processes...
are often found. The high temperature $\alpha$ process is often related to the crystalline fraction. The $\beta$ process in these polymers is related to the amorphous phase and usually represents the glass transition. The low temperature $\gamma$ process is generally considered to originate in the amorphous phase but may also have an important component associated with the crystalline phase. In amorphous polymers the highest temperature relaxation is the glass transition, also referred to as $\alpha$, while $\beta$ and $\gamma$ relaxations also are commonly observed. Of course, in this case these are all associated with the amorphous phase.

The three points of greatest interest in relation to characterizing relaxation processes are (1) determining in what phase they originate, (2) describing the molecular processes underlying them, and (3) relating relaxation behavior to engineering properties and practical applications. DMA and DEA have proved most useful in helping to address these issues. DEA has been used extensively for studying the origin and mechanisms of relaxation processes. However, it is restricted to systems with active dipoles. As a result some relaxation processes that are active mechanically are not active dielectrically (the converse is also true), for example, the $\beta$ relaxations in polyethylene and polytetrafluoroethylene.

**Relaxations That Occur in Amorphous and Crystalline Polymers.**

In isochronal experiments on amorphous polymers, for the temperature interval between the melt and liquid nitrogen temperature, commonly each of the relaxation processes has distinct characteristics related to the specific motions associated with the relaxation processes. The highest temperature or $\alpha$ process is the glass transition involving the cooperative motion of several molecular segments or subunits (between 5 and 10). The glassy-state $\beta$ and $\gamma$ relaxations take place in polymers either with or without flexible side groups and are believed to be due to local rotational motions of the main chain and/or motions of side groups with differing degrees of cooperativity, and a distribution of relaxation times. The sub-$T_g$ relaxations are characterized by an Arrhenius-type temperature dependence of relaxation times. The more complex the cooperative motions associated with a relaxation process, the greater the activation energies. Thus each relaxation process has a different activation energy. This will be discussed further below.

In crystalline polymers there are at least two, and often three, processes observed below the melting point. In polymers that show all three, the high temperature $\alpha$ process commonly is connected with the crystal fraction in the semicrystalline material. The $\beta$ process in such polymers is connected with the amorphous fraction and is the glass–rubber relaxation. In polymers where the $\alpha$ process is not of the above type, it is the glass transition. The low temperature process, $\gamma$ (or $\beta$ where $\alpha$ is missing), is generally agreed to originate in the amorphous phase but may also be affected by the crystalline phase.

There are some generalizations that can be made about the relaxation behavior of the above types (80). Inherently low crystallinity polymers show no crystalline high temperature process but do possess a well-developed amorphous fraction glass–rubber relaxation ($\alpha$). Inherently easily crystallizable, high crystallinity polymers show both $\alpha$ and $\beta$ relaxations where the $\alpha$ relaxation is associated with the crystalline phase. However, the $\beta$ process tends to be less prominent than the amorphous phase $\alpha$ relaxation in the less easily crystallizable polymers.
All crystalline polymers show the low temperature \( \gamma \) (referred to as \( \beta \) when \( \alpha \) is missing) process.

The study of relaxation processes in Semicrystalline Polymers (qv) is a subject of continuing technological interest because of its practical importance. This is based on the observation that the stiffness of typical crystalline engineering thermoplastics at room temperature may be only one-third to one-fifth that of the same material at a low temperature. The drop in stiffness or modulus takes place in regions of temperature associated with a relaxation process.

Similarly, in Amorphous Polymers (qv) the drop in modulus accompanying sub–glass relaxations can have an important effect on engineering properties, particularly brittleness and impact resistance. This is discussed below in a section on impact behavior.

**Effects of Plasticizers and Moisture.** In amorphous polymers the glass transition and the relaxation behavior associated with it are very sensitive to the addition of small amounts of diluents. The relaxation is shifted to lower temperature isochronally or higher frequency isothermally. The usual explanation is that since the diluent molecules are small and mobile, they act to effectively increase the available free volume for segmental motion and hence speed it up. Similar plasticizing effects on the glass–rubber relaxation in crystalline polymers are observed. One example is the case of polyvinyl alcohol (PVOH), which is water-soluble. As shown in Figure 37 (81), PVOH can absorb large amounts of water, which shifts the glass transition to lower temperatures. As the relaxation shifts...
to lower temperatures, it also narrows. The shift to lower temperatures (as noted above) reflects the improved segmental mobility due to additional free volume imparted by the addition of moisture dispersed into the molecular network. The narrowing is likely due to a more uniform distribution of free volume, so that the formerly less-mobile amorphous phase fraction residing near the crystalline interface has become more mobile due to moisture plasticization.

These effects of moisture are also observed in aliphatic polyamides such as nylon-6,6 (82), nylon-6,10 (83,84), and nylon-12 (85), among others. There are three major relaxations in nylon-6,6 (71,82,86,87). The $\alpha$ relaxation is the glass transition reflecting motion in fairly long chain segments in amorphous regions. The $\beta$ relaxation has been attributed to the motion of labile amide groups and may be absent in dry, annealed specimens. The $\gamma$ relaxation has been assigned to motion of short polymethylene segments with some involvement of adjacent amide groups. The addition of small amounts of water or alcohols (which readily dissolve in the amorphous fraction by virtue of hydrogen bonding) moves the $\alpha$ loss peak to lower temperatures (or higher frequencies isothermally) and narrows it, a result similar to that described above for PVOH. Moisture also reduces the temperatures of the $\beta$ and $\gamma$ relaxations to a lesser degree than the $\alpha$ relaxation.

The sorption of water by nylon has a major effect on major mechanical properties of engineering importance. For example, in molded nylon-6,6 at room temperature, the modulus decreases by about a factor of 5, the yield stress decreases by more than half, and there are major increases in the elongation and energy to break as the water content is increased from dryness to saturation (82,88). The reported properties of nylon are frequently those of nylon containing some
amount of absorbed water. Thus, it is important to specify the water content or the relative humidity with which the polymer is in equilibrium.

The dependence of the relaxation temperatures on the level of absorbed water is known from dynamic mechanical studies (82,87,89) as well as dielectric studies (90). The temperature variations with sorbed moisture of the loss modulus peaks for the three relaxations are shown in Figure 38 (82). The test frequency for the three relaxations varies slightly but is around 1 Hz. The data indicate that the temperature of the $\alpha$ relaxation at a given frequency decreases by about 100°C between dryness and saturation. The $\beta$ relaxation is also shifted to lower temperatures and higher frequencies by absorbed water, while the temperature of the $\gamma$ relaxation is only slightly affected, shifting somewhat to lower temperatures and higher frequencies.

In addition, it is found that moisture increases the intensity of the $\beta$ relaxation and reduces its activation energy, as well as decreases the peak height of the $\gamma$ relaxation with little change in activation energy. The decrease in $\gamma$ intensity has been referred to as an “antiplasticization” effect, since it is associated with an increase in modulus and decrease in impact strength. This is discussed further below in reference to impact behavior. The increase in $\beta$ intensity has been associated with the motion of water molecules H-bonded with carbonyl and amide groups about the H-bond axis (84,90).

Moisture is an effective plasticizer for highly polar, phenylene polymers with $\alpha$ relaxations in excess of the 100°C boiling point of water. This is particularly noted in polyamides where strong hydrogen bonding prevents the loss of moisture even at high temperatures up to $T_g$. The polyamide derived from hexamethylene-diamine and a 70/30 mixture of isophthalic and terephthalic acids (nylon 6I/T, 70/30) is quite hydrophillic. A considerable reduction in the dielectric $\alpha$ loss peak

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**Fig. 39.** Effect of moisture content on DMA glass transition of an aromatic poly(amide-imide). Note that a large moisture effect is noted even though $T_g$ is well above the bp of water. — 0.90% water; --, 0.85% water; ---, 2.80% water; <<< 4.25% water (92).
temperature (at frequency of 1 kHz) with increasing moisture content has been documented for this polymer (91). The $\alpha$ peak temperature is a linear function of relative humidity decreasing from 154°C at 0% RH to 60°C at 100% RH. The DSC $T_g$ at 10°C/min decreased from 128°C for a dry sample to 48°C for one conditioned at 97% RH.

The hydrophilic character of nylon 6I/T (70/30) combined with a relatively low permeability to oxygen makes it an attractive candidate as a food-packaging material. The low permeability to O$_2$ is related to the antiplasticization of nylon 6I/T (70/30) by moisture. Moisture in this material decreases the $\gamma$ relaxation strength as in other nylons, reducing the activation entropy for the $\gamma$ process to zero. It is thought that water forms bridges between amide groups that are stable at low temperatures. These bridges serve as effective constraints, reducing the mobility of the adjacent aliphatic segments. Avakian and co-workers (91) contend that the permeability of O$_2$ is associated with the mobility of the aliphatic segments and will therefore decrease with suppression of the $\gamma$ relaxation.

DMA data for samples of an aromatic poly(amide–imide) polymer containing various amounts of moisture are shown in Figures 39 and 40 (92). These data indicate a decrease in $T_g$ of over 100°C at 4.25% moisture sorption. The dry $T_g$ value is around 285°C. Each $\alpha$ loss dispersion has the same shape, indicating that moisture was not lost during the measurement (if moisture were lost, the loss dispersion would broaden because of a gradual shift in the relaxation to higher temperatures during the measurement). Since the $\alpha$ relaxation in this polymer occurs at temperatures well in excess of 100°C, the data show that water is indeed
Fig. 41. Effect of H$_2$O and D$_2$O on the low temperature dielectric $\beta$ relaxation in polysulfone at 1 and 10 KHz (93); circles, H$_2$O; triangles, D$_2$O; closed symbols, 1 KHz; open symbols, 10 KHz. The $\beta$ peak intensity increases as absorbed moisture level increases.

tightly bound in such systems. A broad $\beta$ relaxation at around 100°C is seen to sharpen, increase in intensity, and shift upward to around 140°C in the wet specimens.

The effect of moisture on the $\beta$ relaxations in amorphous phenylene polymers is well documented (93–95) for many of the systems cited previously. For example, Allen and co-workers (93) determined that both the dielectric and mechanical $\beta$ relaxations in polysulfone, polycarbonate, polyphenylene oxide, and polyether sulfone were dependent on the water content of the samples. In addition, the amount of water absorbed depended on the polarity of the molecule. The effect of moisture on the dielectric $\beta$ process in these polymers appears to be greater than for the mechanical loss process, as illustrated in Figures 41 and 42 (93). These results indicate that the absorbed water hydrogen bonds to polar groups along the polymer chain and, as such, takes part in the molecular processes which give rise to the $\beta$ relaxation. This is consistent with the other examples cited previously.

The polymers studied by Allen and co-workers (93) are modestly polar with maximum moisture uptakes of less than 1%. In more polar phenylene polymers such as polyimides (94) and poly(amide–imide)s (92), the mechanical $\beta$ relaxation shows a more significant effect because of the larger amounts (1.5 to >4%) of moisture absorbed.

As in other crystalline polymers the glass–rubber ($\beta$) relaxation in linear or high density polyethylene (HDPE) is sensitive to plasticizing diluents. CCl$_4$ is effective in this regard (96–98). Loss data for HDPE containing absorbed CCl$_4$ such
as those of Figure 43 (96) show a prominent $E''$ peak in the $-60$ to $-80$°C range compared to a very weak (or nonexistent) relaxation peak in the $-30$ to $-50$°C range for the unplasticized material. It is evident that the diluent is effective in removing constraints on the amorphous segments, thus increasing their mobility (reduction in $T_\beta$), and in making more conformations available to reorientation (increase in $\beta$ intensity).

**Impact Behavior.** The Fracture (qv) behavior of polymers under large-scale deformations is of considerable interest for engineering applications of polymers. It is important for material selection to have some practical criteria for decision making. Such criteria are discussed by Menges and Boden (99), who indicate how linear viscoelastic DMA data can be of benefit as a decision-making aid.

The cause of brittle fracture in polymers is the inability of the material to quickly dissipate by molecular relaxation processes the internal stresses generated as a result of the imposed deformation. Brittle fracture occurs when the time to failure is the same order of magnitude (or faster) than the speed of the relaxation process that dominates the mechanical behavior in the temperature range of interest. The relevant relaxation processes are the first $T < T_g$ secondary relaxation ($\beta$ or $\gamma$). A qualitative criterion for determining whether the relaxation will significantly influence the impact properties is whether the isochronal storage modulus (on a log modulus vs $T$ plot) exhibits a distinct step at the damping maximum. The size of the step is related to the relaxation intensity. It has been known for some time that polymers with relatively intense low temperature relaxations may be expected to be “tough” at room temperature (100–102).

The occurrence of a secondary relaxation loss peak by itself is not a necessary and sufficient condition for improved impact strength (99,100). Additional information such as actual impact test data, at temperatures above and below
the relaxation, should be used to verify whether a given relaxation process has a
significant influence on the impact behavior.

Evidence of the importance of secondary ($T < T_g$) relaxations in determining
the impact strength of polymers is provided by numerous examples of changes in
these relaxations by the addition of certain diluents that act as “antiplasticizers.”
The term antiplasticizer relates to the fact that, while these diluents lower $T_g$,
they also cause increases in storage (and tensile) modulus and tensile strength
but lower impact strength and elongation-at-break. Figures 44a and 44b (103)
show storage modulus and tan $\delta$ curves for antiplasticized polysulfone and polycarbonate. As noted previously, both polymers in the pure state have well-defined $\beta$ relaxations at about $-100^\circ C$ (173 K). It is readily apparent that at high diluent levels these relaxations are greatly reduced and virtually eliminated.

The presence of an antiplasticizer in these systems and the resulting near
elimination of the $\beta$ relaxation leads to a higher modulus value at temperatures
above the relaxation range up through room temperature. This also results in
higher tensile strength, lower elongation at break, and reduced impact strength,
as noted in Table 7. Specific volume data suggest a qualitative explanation of
antiplasticization in these systems, where the antiplasticizer molecules fill poly-
mer free volume and restrict the local mode relaxations associated with the $\beta$
relaxation.

Similar observations are found in the case of PVC (104,105), where the addi-
tion of normal plasticizers actually results in antiplasticization until the 15–20%
plasticizer level is reached. At this point modulus and tensile strength begin to decrease because the $T_g$ has been reduced to below room temperature. Pezzin and co-workers (105) show that this antiplasticization effect is closely related to a reduction in the intensity of the $\beta$ relaxation centered around $-40^\circ$C.

We noted previously that various workers (82,85,89,95) have reported similar effects for nylons including nylon-6,6, an amorphous nylon 6I/T (70/30) based on iso- and terephthalic acids, and nylon-12. It was noted that at temperatures below the $\alpha$ relaxation, water is an antiplasticizer for nylon, increasing the modulus and tensile strength and reducing the intensity of the $\gamma$ relaxation. Absorbed water reduces the activation entropy for the $\gamma$ relaxation from a substantial positive
Table 7. Mechanical Property Data for Various Antiplasticized Aromatic Polymer Systems

<table>
<thead>
<tr>
<th>Antiplasticizer</th>
<th>Tensile modulus, GPa&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Tensile strength, MPa&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Elongation at break, %</th>
<th>Izod impact, J/m&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Izod impact, T&lt;sub&gt;g&lt;/sub&gt;, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysulfone-N-phenyl-2-naphthylamine</td>
<td>2.55</td>
<td>75.1</td>
<td>50</td>
<td>80.1</td>
<td>189</td>
</tr>
<tr>
<td>(T&lt;sub&gt;g&lt;/sub&gt; ≈ −16 °C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polysulfone-4,4′-dichlorodiphenylsulfone (T&lt;sub&gt;g&lt;/sub&gt; ≈ 0 °C)</td>
<td>3.18</td>
<td>85.2</td>
<td>7.5</td>
<td>21.4</td>
<td>110</td>
</tr>
<tr>
<td>Bisphenol A</td>
<td>2.28</td>
<td>62.6</td>
<td>50–100</td>
<td>641–854</td>
<td>147</td>
</tr>
<tr>
<td>polycarbonate</td>
<td>2.88</td>
<td>78.6</td>
<td>30.0</td>
<td>69.4</td>
<td>131</td>
</tr>
<tr>
<td>Arochlor 5460</td>
<td>3.06</td>
<td>85.5</td>
<td>6.2</td>
<td>53.4</td>
<td>120</td>
</tr>
<tr>
<td>(T&lt;sub&gt;g&lt;/sub&gt; ≈ 55 °C)</td>
<td>3.31</td>
<td>84.1</td>
<td>9.0</td>
<td>26.7</td>
<td>112</td>
</tr>
</tbody>
</table>

<sup>a</sup>From Ref. 103.
<sup>b</sup>To convert GPa to psi, multiply by 145,000.
<sup>c</sup>To convert MPa to psi; multiply by 145.
<sup>d</sup>To convert J/m to ft·lb/in. (of notch); divide by 53.38.
<sup>e</sup>Determined by measurement on torsion pendulum.
<sup>f</sup>Determined by extrapolation.

value in the dry state to zero at saturation (91,106). It was suggested that this is explained by water forming bridges between amide groups and that these bridges reduce the mobility of the aliphatic segments adjacent to the amide groups. It is known that local mode relaxations of the aliphatic groups in cooperation with the amide groups give rise to the γ relaxation in nylon.

One further note on antiplasticization is that the ability of polymers to be antiplasticized will be related to the strength of their secondary relaxations. Thus, polymers with small relaxations should be unaffected by antiplasticizers (103).

Finally, we consider the question: What determines whether a given polymer will have a secondary relaxation strong enough to impart toughness as described above? This is discussed by Tanaka and co-workers (107), who examined the temperature/frequency dependence of α and β dielectric relaxations in a series of polyarylates with respect to Matsuoka’s cooperative domain model for relaxation (108–110).

The cooperative domain model specifies that when a stress is applied to a polymer, the free energy of the system momentarily increases. As a result, conformers will readjust themselves and shift back to the lower free-energy state. In general, for a conformer to complete a rotational relaxation its nearest neighbors must also rotate in cooperation. However, below the glass transition, polymer segments are pinned in place, making it very difficult for motions to take place. While intermolecular cooperative motions are locked in place during the stress application period, some intramolecular rearrangements are possible between the points along the chain that are pinned by their neighbors. The β relaxation process (or γ in certain cases) involves such motions. Tanaka and co-workers (107) noted that the size of a conformer in the β process is usually equal to the α conformer, such
as for polycarbonate and PET. But in the arylates, with 2,2’-dicarboxy biphenyl groups, the rotation of conformers within a repeat unit becomes nearly impossible when one of the conformers is pinned. Thus, their $\beta$ conformers are often several times larger than their $\alpha$ conformers. Such polymers exhibit very low $\beta$ relaxation intensities and small values for the activation energy. As a result they have low impact strengths and a tendency for brittle behavior.

**DMA Characterization of Cross-Linked Polymers**

**The Glass Transition.** Highly cross-linked polymers are an important class of materials used as adhesives, coatings, and matrices for composites, to name just a few applications. Many of this class are referred to as *thermosets* and almost all are completely amorphous (an exception is the case of liquid crystal thermosets). The glass transition is a most significant parameter for this group and the difficulty in specifying $T_g$ arises from the effect of crosslinking on relaxation in the transition region (79). The general effect on the glass transition by increasing crosslink density is shown in Figure 45. The transition loss dispersion decreases in intensity, broadens, and shifts to higher temperatures. Also, the transition slope of the storage modulus decreases. The broadening of
the relaxation spectrum is further enhanced by network heterogeneity and microphase separation introduced into systems formed from the mixtures of reactive monomers that have different functionalities. The data of Figure 36 for a UV-cured acrylate polymer are representative of such a system.

The highly cross-linked acrylic represented in Figure 36 has a very broad transition region that well illustrates the problem involved in assigning \( T_g \) in such cases. The question to consider is: What criterion do we use for specifying \( T_g \)? The loss dispersion in Figure 36 covers a span of approximately 100°C and is very flat, with no well-defined maximum value. The \( E'' \) maximum which was determined numerically is 70°C lower than the peak \( \tan \delta \). Furthermore, the \( E'' \) peak appears to occur in the transition region above the temperature where \( E' \) begins to decrease gradually from the glassy-state value. Our recommendation in such cases, where the \( T_g \) range is unusually broad, is based on practical considerations. Since network polymers are frequently used in structural applications as adhesives and composite matrix materials, the point where \( E' \) begins to drop from its glassy value is the most appropriate \( T_g \) assignment based primarily on the criterion of retention of structural integrity. This is most easily specified by the onset point, defined by intersection of the tangents to the storage modulus glassy-state curve and transition-region curve.

**Thermoset Cure Characterization by DMA.** On the basis of the information on crosslinking and \( T_g \) noted above, DMA can be used for the cure characterization of Thermosets (qv). There are two aspects of this. First, as the chemical conversion (extent of cure) and the degree of crosslinking advance, \( T_g \) increases. Thus the \( T_g \) measured by DMA correlates with the cure state of the material. In cases where \( T_g \) is not overly broad and a well-defined maximum in the loss modulus is evident, the \( T_g \) value obtained is related to crosslink density. Second, the magnitude of the plateau modulus above \( T_g \) increases with crosslink density. This can be used to estimate the average crosslink density (or molecular weight between crosslinks) of the network. We present a brief review of these issues in the following paragraphs.

It has been shown that in many cases for thermoset systems, there is a quantitative relationship between the chemical conversion of the thermoset and its \( T_g \) value, independent of the time–temperature cure history (111). This is very convenient from an applications standpoint because measurement of \( T_g \) is equivalent to a direct measurement of conversion. It implies that either the molecular structure at a given degree of conversion is the same, regardless of the reaction path, or that differences in the structures produced for different reaction paths do not affect \( T_g \). While a \( T_g \)–degree of cure relationship has been found valid for many epoxy–amine and other thermoset materials, it has been observed not to hold in some cases, which include some epoxy–DICY, cyanate–ester, and phenolic systems. It has also been found not to hold for a given resin system cured by two different methods such as thermal and microwave (112) or thermal and electron beam cures (113).

The reasons why a \( T_g \)–conversion relationship is not valid in some instances are not fully understood. One explanation is that the relationship is not likely to hold under conditions where the cured molecular network has a significant degree of heterogeneity due to composition or molecular weight heterogeneities in the initial monomer, or resulting from phase separation, or even the partial
Fig. 46. DMA isothermal modulus and tan δ vs cure time plot for a supported epoxy resin sample (resin coated onto an inert fiber glass substrate); (a) storage modulus, (b) loss modulus (116).

formation of a liquid crystal phase during polymerization. In the case of the epoxy–DICY and cyanate–ester systems, composition heterogeneity may arise, since the crosslinking agents are catalysts that are added initially as crystalline powders. In such cases there is always some degree of incomplete mixing of the catalyst so that the cross-linked network is heterogeneous, with multiple phases having different crosslink densities occurring on a microscale (114). These phase differences will correspond to local variations in catalyst concentration resulting in local “hot spots.” In the phenolic systems the starting material is generally a mixture of oligomers, with a range of chemical functionalities. This also leads to a heterogeneous cross-linked phase distribution. For practical reasons, in dealing with thermoset cure, it is recommended that $T_g$–conversion data be generated as part of any cure characterization study. This will be useful even if there is not a direct correlation between $T_g$ and conversion. The easiest way to develop a $T_g$–conversion relationship is via DSC. Where degree of conversion cannot be measured directly, $T_g$ is a good means for evaluating cure advancement.

DMA also has been used to determine thermoset vitrification times by running the DMA in an isothermal or temperature-programmed mode that simulates actual processing conditions. The methodology for this is discussed in detail by Prime (115). In general, when thermoset reactions proceed at a given temperature, the uncured thermoset (which may be a solid) is initially converted to a liquid phase before reaction begins. Once the sample is in the liquid phase, crosslinking continues until the viscosity of the system becomes extremely high and the sample passes into the glassy state or vitrifies. At this point the reaction is inhibited due to restrictions on diffusion of reactive groups. So the reaction slows down drastically and, in most instances, essentially stops even though the
chemical reaction is not complete. The increase in storage modulus (which parallels the rise in viscosity) of the system from the onset of reaction can be mapped by DMA either for supported samples (resin coated onto an inert substrate) or unsupported samples. As shown in Figure 46, an isothermal modulus vs cure time plot (116), the storage modulus rises and then levels off at a high value characteristic of the glassy state.

When the modulus reaches its plateau, the polymer has vitrified or attained the glassy state due to the advance of the crosslinking reaction. If the cure reaction is carried out at a temperature $T_i$, the cure reaction continues until the sample vitrifies (becomes glassy) at $T_i$. The effective $T_g$ of the partially cross-linked, vitrified polymer will be equal to or slightly greater than the cure temperature $T_i$ because the reaction rate slows down gradually upon vitrification. If the temperature is then raised above $T_g$, the curing reaction will continue and $T_g$ will gradually increase until the reaction is completed, or $T_g$ again increases to the reaction temperature. If an isochronal DMA scan is run for a partially cured sample, the storage modulus will decrease with temperature at $T_g$ in the usual manner until the reaction starts again. Then the modulus will increase with temperature.

**Dielectric Measurement Methods Applied to Thermoset Cure**

Dielectric analysis (DEA) has the capability for following the transformation of a thermoset from a low molecular weight liquid resin to a solid cross-linked network. In this respect it provides some detail beyond that from a DMA run with supported samples, because it more accurately follows changes that occur in the low viscosity state, as well as during the large viscosity increase leading up to vitrification. Using disposable microdielectric sensors (117), dielectric data can be obtained in the laboratory as well as *in situ* during reactive manufacturing processes with minimal disturbance of the process. Thus, DEA is well suited for process monitoring and process control in real time. DEA can provide information on key characteristics of thermosetting materials, including molecular relaxations, thermal transitions, onset of flow and viscosity minima, rate of cure, and degree of cure. Some of the topics of interest concerning the dielectrometry of thermosets are as follows: (1) ionic conductivity often dominating the observed dielectric properties; (2) the correlation between viscosity and conductivity early in cure; (3) the contribution of dipoles and sample heterogeneities to the measured dielectric properties; and (4) the importance of electrode polarization at low frequencies (118).

We noted previously that in DEA, a sample is placed between two electrodes and a sinusoidal voltage is applied to one of the electrodes. The traditional electrode is a parallel-plate capacitor, as illustrated in Figure 47. The applied voltage establishes an electric field in the sample. In response to this field, the sample becomes electrically polarized and also can conduct a net charge from one electrode to the other. Both the electric polarization and ionic conduction give rise to a current whose amplitude is dependent on the frequency of the measurement and the temperature and structural properties of the medium being tested. The DEA electrode assembly both transmits the applied voltage to the sample and senses the response signals.
Most thermosetting materials possess both permanent and induced dipoles. Static or permanent dipoles consist of inherently polar moieties (not induced by the electric field) within the material, such as amine or hydroxyl groups. The static dipoles, if sufficiently mobile, may rotate in an alternating electric field, thus also storing energy and contributing to the capacitive nature of a material. Even nonpolar polymers can be dielectrically active. In the presence of an electric field, electron clouds may be slightly shifted, inducing a small polarization that is aligned with the electric field. This acts to store energy and contributes to the capacitive nature of a material. These induced dipoles are responsible for nonpolar or symmetrically polar materials having permittivities greater than 2.

Static dipoles also contribute to the loss factor, as can be seen from equation 8. This contribution arises from viscous drag as the dipole rotates through the surrounding medium. As a result of this drag, there can be a significant phase lag between the maximum applied field and maximum dipole deflection. The energy lost because of this phase lag reaches a peak as $\omega$ approaches $\tau^{-1}$. At higher frequencies the dipole hardly moves, because it is not able to keep pace with the changing field, and so little energy is lost, while at lower frequencies the dipole can keep up with the field more easily and, as a result, less energy is expended.

Ionic conduction is the result of current flow due to the motion of mobile ions within the material under test. It has been demonstrated that concentrations well below 1 ppm are sufficient to cause significant ionic conduction levels (118). From equations 7 and 8, it is evident that ionic conduction contributes only to the loss factor and does not affect the permittivity. Epoxy resins typically contain sodium and chloride ions, which are residuals from their manufacture. These impurities are quite sufficient to cause ionic charge transport. Thus, it is common to observe large loss factors in such thermosetting materials when the temperature is above $T_g$, because of the ionic conduction contribution to the loss factor.

An artifact that affects the dielectric properties when ionic conductivity is high is known as electrode polarization. This results from the thermosetting resin acting in combination with the electrodes used to introduce the electric field. Electrode polarization occurs when ionic conduction is extremely high, causing ions...
to collect at the material–electrode interface during a half-cycle of the oscillating electric field. As ions build up at the interface, they accumulate in a thin boundary layer and build up a considerable charge density, and therefore a large capacitance is formed. This has the effect of artificially decreasing the measured values of loss factor and increasing the measured values of permittivity. The measured permittivities attained through electrode polarization are usually large enough (greater than 100) to render electrode polarization easy to identify. A detailed discussion of the electrode polarization effect is given in Reference 75.

There are two electrode sensor geometries that are common in dielectric analysis. As noted previously, the traditional electrode is a parallel-plate capacitor (Fig. 47). However, this geometry is not well suited for thermoset cure monitoring. In order to obtain high signal levels with the classical parallel-plate technique, thin specimens with large areas are required, and the dielectric properties are an average of the bulk. In addition, low frequency measurements, which can reveal much about glass transitions and the mechanical properties of the material, are often difficult to obtain using the parallel-plate technique, since the signal current is proportional to the test frequency. The principal disadvantage, however, is the need to accurately control or measure the plate spacing. Thermosets during cure frequently undergo dimensional changes due to temperature, reaction-induced shrinkage, or pressure. In order to obtain quantitative values for the dielectric properties, the plate spacing must be known throughout the experiment.

The interdigitated or comb electrode (117) is a contemporary, alternative geometry, as illustrated in Figure 48. For this type of sensor, metal electrodes are fabricated on an insulating substrate by photopatterning. The substrate is typically a ceramic or a silicon integrated circuit. Sampling is simplified. Either a small amount of sample is placed over the electrode sensor, or the sensor may be embedded in the test medium. The comb electrode has been miniaturized as a microdielectric sensor, which combines the electrode with a pair of field-effect transistors in a silicon, integrated microcircuit. For thermosets these microsensors circumvent the problems associated with parallel-plate capacitors while
achieving comparable sensitivities. The microsensor is small, around 0.5 in. in size. This design permits a one-sided, very localized measurement of dielectric properties, is particularly well suited for thin films, and can be inserted directly into a part being cured. The modern measurement circuitry also circumvents the traditional lower frequency limits, thus permitting dielectric analysis at frequencies as low as 0.001 Hz. Very fast response times of considerably less than 1 s are possible so that the microsensors can monitor very fast reactions.

**Dielectric Analysis of Thermoset Glass Transitions.** As a polymer is heated through its glass transition, static dipoles gain mobility and start to oscillate in the electric field. This causes an increase in permittivity, with a corresponding loss factor peak. At the low temperature side of the glass transition, dipoles are able to respond only to low frequency excitation, because their mobility is low. Dipole mobility increases as the polymer is heated through $T_g$ and above. Charged ions also gain mobility as a material is heated through $T_g$ and will start to contribute to conductive losses above $T_g$. The contribution of conductive losses to the measured loss factor may be large and can often overshadow the smaller dipole loss contributions. The loss dispersion observed in dielectric measurements is analogous to that observed for mechanical measurements. Low frequency dipole loss peaks (less than 1 Hz) correspond well to other thermal analysis measurements of $T_g$.

Figure 49 shows temperature-dependent data for the permittivity and loss factor of a diglycidal ether of bisphenol A (DGEBA) epoxy resin in the vicinity of its glass transition ($T_g = -17^\circ C$), measured at frequencies between 0.1 and 10,000 Hz (118). At temperatures well below $T_g$, the permittivity at all frequencies has a value of 4.2 (the unrelaxed permittivity, $\varepsilon_u$) and the loss factor is less than 0.1. As the temperature approaches $T_g$, the dipoles gain sufficient mobility to contribute to the permittivity, with evidence of this mobility increase occurring first at the lowest frequency. With a further increase in temperature, the permittivity for each given frequency levels off at the relaxed permittivity $\varepsilon_r$, and then decreases because of increasing temperature (118). This is then followed by an abrupt increase in $\varepsilon''$ as a result of ionic conductivity and electrode polarization. At each frequency, a dipole peak is observed in the loss factor at $T_g$. $\varepsilon''$ then rises continuously with temperature because of an increase in ionic conductivity. The frequency at which the dipole loss peak occurs is proportional to the ionic mobility. Both the frequency of the loss factor maximum and the ionic conductivity increase by many orders of magnitude over a narrow temperature range, a characteristic of relaxation processes very close to the glass-transition temperature. Note in Figure 49, that the 0.1-Hz loss peak temperature is similar to the $T_g$ as measured by DSC ($-17^\circ C$). A similar correlation was observed between the onset of the modulus decrease by DMA at 0.1 Hz and the $T_g$ as measured by DSC (119).

**Cure Characterization.** With considerations concerning the DEA observations related to $T_g$ in mind, it is apparent that dielectric properties can be particularly useful in following chemical and physical changes in real time during thermoset cure. At the beginning of cure, the dipole relaxation time is much shorter than the cycle time, and the dipoles and ions move easily and align themselves with the field as the polarity changes, as illustrated in Figure 50a. Hence, both the permittivity and the loss factor have high values initially. As cure proceeds, crosslinking produces larger and more complex molecules and the viscosity
Fig. 49. Temperature-dependent data for the permittivity and loss factor of an uncured DGEBA epoxy resin (Epon 825) in the vicinity of its glass transition \(T_g = -17^\circ C\), measured at frequencies between 0.1 and 10,000 Hz (118).

of the medium increases. This restricts the motion of the dipoles and ions and causes an increase in the relaxation time. If the frequency of the electric field is fixed, then the relaxation time will approach the cycle time, and there will be less alignment of dipoles and less ion transport, as shown in Figure 50b. Eventually, as the relaxation time becomes large relative to the cycle time, the dipoles will be randomly oriented, as illustrated in Figure 50c. Concomitantly, as the curing polymer becomes more viscous and/or glassy, it offers increasing resistance to the motion of free ions, and ion mobility decreases. This results in both a low permittivity and a low loss factor.

During cure, \(\varepsilon''\) generally will change by several orders of magnitude. As a result, \(\varepsilon''\) is a particularly useful function for evaluating the progression of cure. The loss factor can be expressed as

\[
\varepsilon'' = \varepsilon''_d + \frac{\sigma}{\omega \varepsilon_0} \tag{10}
\]

where \(\varepsilon''_d\) is the energy loss arising from dipole orientation, and \(\sigma, \omega,\) and \(\varepsilon_0\) are as previously defined in equations 7 and 8. At low frequencies, the conductivity term
will usually be considerably larger than the dipole term, and the value for conductivity, $\sigma$, then can be extracted from the loss factor by equating $\sigma$ to $\varepsilon''/\omega\varepsilon_0$. The ionic conductivity is very useful for distinguishing frequency-dependent dipolar phenomena, such as the glass transition, from frequency-independent phenomena, such as the onset of flow and the viscosity minimum.

**Examples and Applications of DEA in Curing of Thermosets**

Valuable information about the molecular and rheological behavior of thermosets during processing can be obtained from DEA, particularly for on-line cure monitoring and process control. This is illustrated in the following example representing the cure of a DGEBA/diaminodiphenylsulfone, epoxy–amine system (DGEBA/DDS).

The permittivity change measured over a range of frequencies during the isothermal cure of a DGEBA/DDS resin is shown in Figure 51 (120). The cure temperature is $137^\circ C$. To a first approximation, these data are the mirror image of those in Figure 49, consistent with the idea that the change in dielectric properties due to crosslinking during isothermal cure is similar to the effect of a decrease in temperature at fixed $T_g$. Examination of Figure 51 shows an
important difference between the temperature and cure time dependencies, namely, that the relaxed permittivity continues to decrease with cure time under isothermal conditions. This is a direct result of the changing chemistry. The permittivity decreases during cure because of the decreasing ability of the molecules (dipoles) to completely align during the cycle time. Early in the cure at long cycle times (i.e., at low frequencies), the measured permittivity is high because of electrode polarization (121). The relaxed permittivity $\varepsilon_r$ (i.e., the maximum dipole alignment that can be achieved, assuming no electrode polarization) is indicated by the shoulder early in the polymerization at high frequencies. The relaxed permittivity for this system is $\sim 14$. As cure proceeds, the dipoles find it more difficult to align themselves with the periodic field and an unrelaxed permittivity, $\varepsilon_u$, of $\sim 4$ is achieved. The loss factor during cure is also illustrated in Figure 51. $\varepsilon''$ is a function of the energy required for both dipole orientation and ionic conduction. Early in the cure, $\varepsilon''$ is inversely proportional to the frequency $\omega$ (see eq. 10), indicating that ion mobility dominates the loss factor. In Figure 51, the conductivity $\sigma$ can be seen to decrease (eq. 11) with cure because of the increasing viscosity of the resin. This decrease is followed by a peak in $\varepsilon''$. Here the highest frequency peak occurs at the shortest time. This loss peak is due to the restriction of dipole
rotation in the cross-linked resin, and its maximum has been correlated with vitrification (120,122). Similar dielectric relaxation results during isothermal cure have been reported for a DGEBA/DDM (diaminodiphenyl methane) resin (121). Corresponding measurements may be made by dynamic mechanical analysis (see Figs. 52 and 53).

Fig. 52. Dynamic mechanical storage modulus data measured over a range of frequencies during the isothermal cure (137°C) of the same epoxy–amine system (DGEBA/DDS) as in Figure 51 (120).

Fig. 53. Dynamic mechanical loss modulus data measured over a range of frequencies during the isothermal cure (137°C) of the same epoxy–amine system (DGEBA/DDS) as in Figure 51 (120).
Fig. 54. Isothermal ionic conductivity data for the DGEBA/DDS resin of Figure 51 at various cure temperatures (76,120). Θ, 135 °C; ◆, 145 °C; ▲, 162 °C; Δ, 167 °C; ●, 173 °C; ×, 188 °C.

From equation 11, the ionic conductivity ($\sigma$) can be calculated from the frequency-independent portion of the loss factor data, that is, where a log-log plot of loss factor versus frequency has a slope of $-1$, using the relation

$$\varepsilon’’ = \frac{\sigma}{\omega \varepsilon_0} \tag{11}$$

Conductivity versus reaction time data for the isothermal cure of the DGEBA/DDS epoxy at six different cure temperatures are shown in Figure 54 (123). If the ion concentration does not change during cure, then $\sigma$ is directly proportional to ion mobility. Early in the reaction, the ionic impurities move freely in the system and the ionic conductivity is high. The ionic conductivity decreases as the cure proceeds and viscosity increases, offering more resistance to the transport of ions. Hence, conductivity is related to the viscosity of the polymer system (124) and the density or “tightness” of the crosslink network. Eventually, there is an inflection in the conductivity versus cure time curve that marks the slowing of the reaction. When there is no further change in conductivity with cure time (ie, $d\sigma/dt \rightarrow 0$), the reaction is considered to be complete (125).

As noted above the ionic conductivity is related to the viscosity of the system prior to up to vitrification, where the reaction becomes diffusion-controlled (126). This is demonstrated by observing conductivity and viscosity changes during dynamic curing at a constant heating rate. Figure 55 illustrates the dynamic cure of a brominated epoxy–phenolic system at a heating rate of 7°C/min (125). Superimposed on the dielectric loss factor plot are dynamic viscosity data taken in a rheometrics rheometer specially adapted to simultaneously measure both dielectric and flow properties of a curing resin. At short times (corresponding to low
Fig. 55. Dynamic cure of a brominated epoxy–phenolic system at a heating rate of 7°C/min (125); superimposed on the dielectric loss factor plot are dynamic viscosity data taken with a rheometrics rheometer. 1 Pa · s = 10 P.

temperatures), where the reaction is insignificant, the loss factor increases with temperature because of decreasing viscosity. After ~18 min of ramped heating, the reaction rate becomes significant, resulting in a viscosity increase, while conductivity decreases. The loss factor maximum peak is frequency-independent and occurs in the same time range as the minimum viscosity. In addition, frequency-dependent dipole peaks preceding the loss factor maximum correspond to the softening of the resin system upon heating as the neat resin passes through the glass transition. The dipole peaks observed following the loss factor maximum occur near the time at which the torque input overloads on the rheometer, indicating that they correspond to vitrification (127,128). Similar studies were reported for a bismaleimide–triazine resin system (129).

Figure 56 shows the results of dielectric analysis for the DGEBA/DDS system at a heating rate of 3°C/min, presented as log ε” versus temperature. The glass transition is detected by the frequency-dependent dipole peaks (Fig. 56b) between 0 and 50°C (T_g by DSC would be more typical of values at 0.1–1 Hz, perhaps 20–30°C lower than these data) (76). The frequency-independent viscosity minimum is also evident near 150°C.

For more detail on DEA characterization of thermoset cure as well as other aspects of thermosets, the reader is referred to the excellent presentation by
Fig. 56. Dielectric analysis data for the DGEBA/DDS system at a heating rate of 3°C/min, presented as log ($\varepsilon''$) vs temperature. The glass transition is indicated by the frequency-dependent dipole peaks between 0 and 50°C (76).

Prime (115) and the entry on thermosets by Prime and Gotro in this encyclopedia.

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DIELECTRIC RELAXATION

Introduction

The control of dielectric permittivity and loss of solid polymers, through an understanding of the origins of their dipole relaxation and ionic conduction processes, is essential for their use in electrical insulation, in electrical/electronic circuits, and...