Dielectric Analysis: The Technique

Dielectric Analysis (DEA) measures the two fundamental electrical characteristics of a material - capacitance and conductance - as a function of time, temperature, and frequency. The capacitive nature of a material is its ability to store electric charge, and the conductive nature is its ability to transfer electric charge. While these electrical properties are important in themselves, they have even more significance when correlated to molecular activity. Such correlation allows the chemistry, rheology (flow), and molecular mobility (relaxation) of viscoelastic materials to be studied.

What DEA Can Tell You
- Permittivity
- Loss factor
- Glass transition temperature
- Degree of cure
- Rate of cure
- Ionic conductivity
- Secondary transition temperatures
- Polymer morphology

Uses of DEA

Research and Development
- Theoretical research on new materials and processes
- New materials development
- Formulation optimization
- Applications development
- End-use performance prediction
- Competitive product evaluation

Quality Control/Assurance
- Vendor certification
- Incoming/outgoing material consistency
- Process optimization
- Heat history tracking
- Finished product performance
- Troubleshooting
TA Instruments DEA 2970 Dielectric Analyzer

The TA Instruments DEA 2970 Dielectric Analyzer further extends the materials characterization capabilities of TA Instruments thermal analysis systems. It complements the traditional techniques by allowing the scientist to view molecular motion from a different perspective, that is, through changes in electrical properties. The results provide both thermal and rheological information.

In thermal analysis experiments, the DEA heats and/or cools samples in order to identify thermal transitions. For some measurements, it has extremely high sensitivity to changes in physical properties, which makes it possible to detect transitions that are not visible by other techniques. For example, DEA is more sensitive than differential scanning calorimetry (DSC) for analyzing the later stages of cure, and its ability to easily evaluate liquids is an advantage over dynamic mechanical analysis (DMA).

For rheological studies, the DEA is particularly effective because it can monitor the movement of ions in a material. A single dielectric test can identify key events affecting rheological changes: the time and temperature which correspond to minimum viscosity, the onset of flow, onset of cure, maximum rate of reaction, and completion of cure. While dielectric analysis does not provide absolute values for viscosity, the shape of the dielectric curves usually can be correlated directly to the viscometer profiles of curing resins.

Analysts will find that DEA data together with complementary data from DSC and DMA, as noted above, as well as thermogravimetric analysis (TGA) and thermomechanical analysis (TMA) data gives them a more complete understanding of the internal structure and performance characteristics of materials.

Hardware

The DEA 2970 dielectric analyzer is an add-on module for any of the TA Instruments Thermal Analyst Systems. It consists of a sensor and ram/furnace assembly (Figure 1), incorporated in a cabinet which contains the supporting electronics. There are four types of sensors (Figure 2) - ceramic parallel plate, ceramic thin film, ceramic single surface, and remote single surface - which are interchangeable and disposable. The system's exceptional versatility permits analysis of bulk or surface properties, using milligram or full-size product samples (e.g. in a laboratory oven, a large part in a molding press or sheets of prepreg in storage). Sensor disposability not only is a convenience and ease-of-use feature, but makes possible the measurement of hard-to-handle samples.

The ceramic sensors are mounted in the ram/furnace assembly, which provides all the necessary environmental conditions: controlled heating and cooling, atmosphere, and applied force. The ram, driven by a stepper motor, applies a constant force or maintains a constant plate spacing, based on information from a force transducer and a linear variable differential transformer (LVDT). This assures desired electrode spacing and optimum surface contact with the sample. Sensor insertion and removal are quick and easy, requiring no tools, fasteners or soldering. All electrical contacts are made automatically.

The remote single-surface sensor* consists of a flexible ribbon cable with a microdielectrometer sensor at one end and a connector at the other. The sensor end is designed to be embedded in a sample; the connector end is for attachment to the instrument.

The module cabinet contains the electronic circuits and software for experiment control and data handling, a keyboard/display for local control of operation, and a GPIB interface for communication with the controller.

The controller is an essential component of the complete DEA system. It is used to program experiments, analyze results, and customize reports. A plotter is required for preparation of hard copy reports.

* The remote single-surface sensor is a product of Micromet Instruments, Inc., Newton Centre, MA, and is provided to TA Instruments for use with the DEA 2970.
**Electronics**

The heart of the DEA system is its electronic circuitry and software.* They implement the theory of the technique and give life to the hardware, making the system effective, practical, accurate, and fast. Results are produced almost instantaneously.

One key to the effectiveness of the DEA 2970 is its measurement technique, which avoids the limitations inherent in instruments based on a Wheatstone bridge. This makes possible accurate measurements at low frequencies as well as high frequencies, and contributes to the instrument’s operating speed.

Precision and accuracy are further assured by complete factory calibration of the measurement electronics.

Design of the electronic system is depicted in Figure 3. Components of the system and their functions are:

**Controller/Analyzer:** This is the operator’s primary interface with the instrument. It is used to program experiments and analyze results. The DEA module can be operated from all of the TA Instruments Thermal Analyst Controllers.

**Module Microprocessor:** A microprocessor/computer is the heart of the module’s operating electronics. Located in the DEA module, it controls all instrument functions, including operation of the experiment, mathematical manipulation of data, and communication with the controller.

**Frequency Generator:** The frequency generator synthesizes a specific, high-purity sine-wave signal to establish an electrical field and excite the sample. The computer memory stores a 32K-point sine-wave generation table. Each point is a 16-bit number, which gives a signal resolution of 1 part in 64,000.

**Electrodes:** The input frequency signal at a specified voltage is applied to the sample through the input electrode. The output electrode receives the response current from the sample.

**Response Interface:** An electronic interface reads the measured response current generated by the sample, amplifies the signal, and sends it to the A/D converter. It also feeds the signal back to the guard ring on the response electrode (and to the cable shielding) to assure voltage equilibrium with the electrode, and thus prevent current leakage.

**A/D Converter:** The A/D converter transforms the amplified analog signal to a digital format.

**Digital Signal Processor (DSP):** Signals from the A/D converter and information about the input voltage are used by the DSP to determine the in-phase and out-of-phase current.

The processed phase and gain signals are then sent back to the Module Microprocessor, where they are combined with sample-thickness measurement signals from the LVDT to calculate permittivity ($\varepsilon''$) and loss factor ($\varepsilon''$).

The entire process - from frequency generation to final calculations - takes place almost instantaneously, making meaningful results available in real-time. They can be read on the controller screen or the module display.

* The DEA incorporates technology licensed to TA Instruments by Micromet Instruments, Inc., Newton Centre (MA).
**Dielectric Theory**

Dielectric analysis measures the two fundamental electrical characteristics of a material - capacitance and conductance - as a function of time, temperature and frequency. The capacitive nature of a material is its ability to store electric charge, and the conductive nature is its ability to transfer electric charge. While these electrical properties are important in themselves, they have even more significance when they are correlated to molecular activity. Such correlation allows the scientist to probe the chemistry, rheology (flow), and molecular mobility (relaxation) of polymeric materials.

Four major properties are reported during dielectric analysis:
- \( \varepsilon' \) = permittivity (also called dielectric constant)
- \( \varepsilon'' \) = loss factor
- \( \tan \delta \) = dissipation factor \( \varepsilon''/\varepsilon' = \tan (90^\circ - \theta) \)
- \( \sigma \) = ionic conductivity

\( \varepsilon', \varepsilon'' \) and \( \tan \delta \) are dimensionless. Ionic conductivity has dimension in mhos/cm, i.e., \((\text{ohm-cm})^{-1}\). \( \varepsilon' \) is proportional to capacitance and \( \varepsilon'' \) is proportional to conductance. Ionic conductivity is derived from measurement of \( \varepsilon'' \).

The actual DEA measurement (parallel plate) involves placing a sample between two gold electrodes and exposing it to an alternating electrical field (Figure 4). The field is created by applying a sinusoidal voltage to one of the electrodes. This produces polarization within the sample, causing oscillation which is at the same frequency as the field but with a phase angle shift (\( \theta \)). The phase angle shift is measured by comparing the applied voltage to the measured current (Figure 5). The measured current is separated into capacitance and conductance components, using the relationships shown in Figure 6. Values for these components are calculated by the equations:

\[
\begin{align*}
\text{Capacitance (C)} = & \left( \frac{V_{\text{measured}}}{V_{\text{applied}}} \right) \sin \theta \\
\text{(farads)} = & \left( \frac{1}{2 \pi f} \right) \\
\text{Conductance (mhos)} = & \left( \frac{1}{R} \right) \left( \frac{V_{\text{measured}}}{V_{\text{applied}}} \right) \cos \theta \\
\end{align*}
\]

Where: \( f \) = Applied frequency (Hz) \\
\( R \) = Resistivity (ohms)

Permittivity (\( \varepsilon' \)) and loss factor (\( \varepsilon'' \)) both provide valuable information about molecular motion. \( \varepsilon' \) measures the alignment of dipoles, while \( \varepsilon'' \) represents the energy required to align dipoles and move ions. Dipole alignment and ion behavior in an electrical field are shown schematically in Figure 7.
A dipole can be represented as a chemical bond which has an unbalanced distribution of charge in a molecule. One part is partially negative and the other partially positive. Permanent dipoles exist in the absence of an applied electric field, and are due to the differences in electronegativity of the bonded atoms (e.g. carbonyl bond $C=O$, $C-N$, etc.). Induced dipoles are those created by the applied electric field which causes redistribution of electrons shared between bonded atoms with similar electronegativity.

Values for $\varepsilon'$ and $\varepsilon''$ are calculated by equations which quantify these relationships:

\[
\varepsilon' = \text{permittivity due to induced dipoles} + \text{permittivity due to alignment of dipoles}
\]

\[
\varepsilon'' = \text{dipole loss factor} + \text{ionic conductance}
\]

$\varepsilon'$ represents the amount of alignment of the dipoles to the electric field. $\varepsilon'$ is low for polymers at low temperature (i.e., below thermal transitions) because the molecules are frozen in place and the dipoles cannot move to align themselves with the electric field. For the same reasons, $\varepsilon'$ is low for highly crosslinked resins.

$\varepsilon''$ measures the amount of energy required to align dipoles or move ions. Ionic conduction is not significant until the polymer becomes fluid (e.g., above the glass transition or melting point). Therefore, $\varepsilon''$ represents the energy required to align dipoles below and through Tg. $\varepsilon''$ displays a peak as the polymer passes through the Tg. Above the Tg, $\varepsilon''$ is used to calculate the bulk ionic conductivity, using the equation:

\[
\sigma = \varepsilon'' \omega \epsilon_0
\]

where:

- $\sigma$ = ionic conductivity
- $\omega$ = angular frequency ($2\pi f$)
- $f$ = frequency (Hz)
- $\epsilon_0$ = absolute permittivity of free space ($8.85 \times 10^{-12}$ F/m)

Bulk ionic conductivity ($\sigma$) can be used to follow the rheological changes that take place during the processing of thermoplastics and the curing of thermosets. Ionic conductivity has been directly correlated with viscosity, because fluidity is indicated by the ease with which ionic impurities can migrate through the sample.
**Principles of Operation**

A complete dielectric analysis system requires the DEA 2970 module*, a Thermal Analyst controller/analyser and a plotter for preparation of hard copy reports.

**Programmer/Controller/Analyzer**

The controller/analyser is used for programming an experiment, performing other operator-programmable control functions, and analyzing data. With it, the operator establishes all conditions and parameters for an experiment, such as method, temperature program, sample spacing, and force. These instructions are transmitted to the module’s operating software, which is resident in a microprocessor located in the electronics base of the DEA module. The microprocessor also contains programming for mathematical calculations, data manipulation, and calibration factors.

During an experiment, the module’s keyboard/display unit can be used as a local control center for controlling the position of the ram, starting or stopping the experiment, or displaying current status.

**Ram/Furnace Assembly**

The furnace (Figures 8 and 10) contains a mica-clad Inconel heater attached to a silver block and surrounded by a channel for liquid-nitrogen cooling to subambient temperatures. The computer controls the heating or cooling rate and liquid nitrogen flow. A recess at the bottom of the furnace seats the bottom parallel-plate sensor or ceramic single-surface sensor. A metal drip pan is used as a furnace liner to prevent contamination and assure easy cleanup.

The rams are plug-in, modular devices. Two different rams are offered, one for use with the parallel-plate sensor and thin film sensor (Figure 8), the other for the single-surface sensor (Figure 10). Both contain spring-loaded probes to make electrical contact with the sensors positioned on the surface of the furnace cavity. The parallel-plate ram also seats and provides electrical contacts for the top parallel-plate sensor. A cylindrical plunger connected to an LVDT measures sample thickness during the experiment. The ram assembly is secured to a top plate, which in turn is attached to three metal posts connected to the ram motor, located under the furnace. Ram operation is controlled by the operating software, and uses inputs from the force transducer and LVDT to monitor applied force and sample thickness. The operator can program for limits based on minimum plate spacing and/or maximum force. By monitoring these variables, it is possible to obtain accurate test data on a sample even after it has undergone dramatic changes in physical form, such as melting or curing. Ram covers are provided to protect rams from contamination by samples and to help make cleanup easy.

**Electrodes/Sensors**

In a dielectric analysis experiment, a sample is placed in contact with electrodes and subjected to an applied sinusoidal voltage. Sample response is measured as a function of time, temperature, and frequency. The electrode assemblies serve two purposes: transmitting the applied voltage to the sample, and sensing the response signals. The different geometries of the sensors makes possible the measurement of bulk or surface properties for a wide variety of solid, paste, and liquid materials. There are four types of electrode/sensors.
Ceramic Parallel Plate: The parallel-plate sensor (Figure 9) uses two gold-plated electrodes in parallel to evaluate bulk dielectric properties in a material and to track molecular relaxations. The lower electrode, positioned at the bottom of the furnace, applies the voltage which sets up the electrical field and polarizes the sample. The upper electrode, attached to the face of the ram, measures the generated current, which is then converted to an output voltage and amplified. A guard ring around the perimeter of the upper electrode prevents electric-field fringing and stray capacitance at the edge of the plates. The electrodes are screen-printed gold on ceramic substrates. A platinum resistance temperature detector (RTD) around the circumference of the bottom electrode continuously measures sample temperature. Signal circuits are connected through pads on the lower sensor which are contacted by spring-loaded probes attached to the ram. Accuracy and reproducibility are assured because plate spacing and force on the sample are continuously measured and controlled during the experiment. This corrects for sample expansion/contraction and maintains good electrode/sample-surface contact.

Ceramic Thin Film: The ceramic thin film sensor is a variation on the standard parallel plate configuration. When evaluating materials in the parallel-plate mode, it is critical to maintain direct contact between the material surface and the sensor. Dry nitrogen, which is normally used as the purge gas during DEA experiments is a good dielectric material. Thus any nitrogen present at the sample/measurement electrode interface creates an interference that affects results. Obviously, this effect is more noticeable with thin films since the interfering nitrogen layer becomes a more significant portion of the region being evaluated.

One way to improve sample/measurement electrode contact is to sputter coat, under vacuum, a metallic electrode directly onto the sample surface. In sputter coating, the sample is placed in a vacuum to remove any interfering gas molecules. The sample surface is then exposed to a plasma of metal ions (usually gold) which deposits onto the sample surface. This forms a conducting layer on the sample that provides excellent contact with the DEA measurement electrodes.

The sensor electrode area can now be smaller because it is only a contact point. The guard ring can be eliminated since edge (fringing field) effects are negligible.

Ceramic Single Surface: The ceramic single-surface sensor (Figure 11) is used for surface-property evaluation and curing experiments. Sensor design is based on a co-planar, interdigitated-comb configuration of electrodes (Figure 12). The assembly consists of a ceramic substrate, metal ground plate, high temperature insulating layer, screen-printed gold electrode arrays, a platinum resistance temperature detector (RTD), and electrical contact pads.

In an experiment, the sensor is placed face up at the bottom of the oven and the sample positioned on its surface. Ram pressure causes the sensor to embed in the surface of the sample. This forces sample material to flow into the spaces between the electrodes. Since the channels are precisely 125 μm wide and 12.5 μm deep, electrode spacing and sample thickness are predetermined, assuring intimate sample/electrode contact. Spring-loaded electrical probes attached to the ram make contact with pads on the sensor, completing the signal circuits. The output current is measured, then amplified and converted to an output voltage. Gain and phase data are sent to a calibration table stored in computer memory, where they are used to determine $\varepsilon'$ and $\varepsilon''$. 
Remote Single Surface*: Because the remote sensor is designed with flexible, ribbon-cable leads, it can be embedded in a sample of any size for testing outside the ram/furnace assembly. In this mode, it can be used to measure either bulk or surface properties. Applications include monitoring dielectric properties of a polymer during molding or while exposed to adverse environments such as solvents or ultraviolet light. It is also possible to embed the sensor in a full-sized product for long-term testing of end-use performance, or in an intermediate-stage material for monitoring of stability and heat history during storage and shipping. In such uses, the sample and embedded sensor are periodically returned to the instrument for evaluation.

Construction of the remote single-surface sensor is shown in Figure 13. The co-planer, interdigitated-comb design of the electrodes is similar to that of the ceramic single-surface sensor, but the sensing area is considerably smaller. The channels are 12.5 μm wide and 0.75 μm deep, thus allowing analysis of very thin coatings and surfaces. The electrodes are arrayed on a silicon substrate supported by a polyimide-film carrier and connected to copper conductors in the ribbon cable. The flexibility of the cable and small sensor size, together with the use of a single amplifier (in the integrated circuit adjacent to the sensor array) allow the sensor to monitor a sample up to 10 feet away from the instrument. Sample temperature is measured by a thermal diode adjacent to the sensing array. Gain and phase-angle data are sent to a stored calibration table for determination of values for \( \varepsilon' \) and \( \varepsilon'' \).

Remote sensor assemblies are available in cable lengths up to 10 feet. The cable’s connector attaches to the instrument through an interface on the front of the module.

* The remote single-surface sensor is a product of Micromet Instruments, Inc., Newton Centre (MA), and is provided to TA Instruments for use with the DEA 2970.
Features and Benefits

TA Instruments DEA 2970 Dielectric Analyzer is a versatile instrument for characterizing the thermal and electrical properties of materials. The DEA 2970 provides essential information which complements that available from other thermal analysis techniques.

Major benefits of a DEA 2970 system and the features which make them possible include:

Testing Versatility

- **Four types of interchangeable, disposable sensors**: See pgs. 7-9

- **Wide temperature range**: Testing capability from -150°C to 500°C allows evaluation of low temperature transitions in materials, as well as higher temperature phenomena such as curing. Ramp, step, or isothermal heating methods are operator-selectable at rates from 0.01 to 50°C/minute.

- **Wide frequency range and frequency multiplexing**: The DEA 2970 provides more than 7 decades of frequency (0.003-100,000Hz) and the ability to multiplex up to 28 individual frequencies per experiment, thus facilitating a more complete assessment of rheological behavior from a single experiment. Frequency selection is totally operator selectable.

- **Automatic calibration**: System calibration includes the dielectric sensors, temperature sensor, force transducer, and LVDT. Results are stored and automatically applied to all subsequent measurements.

- **Fast, automated testing**: Many DEA experiments require less than one hour. Tests that take longer can be programmed for automatic control, freeing the operator for other tasks.

- **Wide range of sample geometries**: The DEA 2970 accommodates samples in solid, thin film, powder, paste or liquid form (See Figure 14). Only a few milligrams of sample are necessary to make a measurement. Larger test samples can be evaluated with the remote single-surface sensor in special environments such as a hot press.

- **Variable sample force**: Ability to subject the sample to a constant force (in the range 5-500 Newtons) during the experiment ensures that the sensor maintains good contact with the sample even if the sample softens and flows. As an alternative, a constant sample thickness (sensor electrode) spacing can be chosen for evaluating liquid samples.

- **Automated cooling**: Use of the autofill liquid nitrogen cooling accessory (LNCA) allows unattended operation of the DEA, as well as providing rapid cool down between experiments. The autofill LNCA is also compatible with the TA Instruments DSC and DMA modules.

Data Analysis Versatility

The DEA 2970 with a TA Instruments Thermal Analyst Controller and DEA Standard Data Analysis software forms a complete system designed to collect, store, retrieve, analyze, and print/plot all important viscoelastic and rheological data from an experiment. In the process, the raw data is automatically transformed into fundamental units of measure which are easy to understand and apply. The sidebar on the next page lists the experimental variables and analyzed properties offered by the DEA 2970.
System Compatibility
The DEA 2970 is one of the broad family of thermal analysis techniques compatible with the Thermal Analyst Controllers. Together, these techniques constitute the most complete system available for the characterization of materials. The other techniques available include:

- Differential Scanning Calorimetry (DSC)
- Modulated DSC (MDSC)™
- Pressure DSC
- Dual Sample DSC
- Differential Photocalorimetry (DPC)
- High Temperature Differential Thermal Analysis (DTA)
- Thermogravimetric Analysis (TGA)
- High Resolution Thermogravimetric Analysis (Hi-Res™ TGA)
- Simultaneous TGA-DTA
- Thermomechanical Analysis (TMA)
- Dynamic Mechanical Analysis (DMA)

As part of a Thermal Analyst system, the DEA 2970 benefits from the methods versatility, multitasking, and multi-module capabilities inherent in the controller. Up to 15 experimental methods containing up to 60 segments selected from 18 available functions, including control of heating/cooling, environment, and data handling can be stored in the controller for recall and use. Once the experiment is set up and initiated, all functions are performed automatically.

Multitasking capability allows the operator to perform several tasks simultaneously: (1) collect data from current experiments, (2) view or plot real-time data, (3) analyze and plot data from a previous experiment, and (4) set up instrument conditions for the next experiment. In addition, with multimodule capability, the Thermal Analyst Controller can control up to 3 other modules while running DEA experiments. The net result is a DEA system that delivers superior performance and unmatched productivity.

Measured Test Variables
- Frequency
- Amplitude
- Phase Angle
- Force
- Time
- Temperature
- Thickness

Calculated Properties*
- Permittivity (ε’)
- Loss Factor (ε”)
- Tan Delta (δ)
- Complex Permittivity (ε*)
- Conductivity (σ)

Figure 15
All module parameters are operator selectable.

* All calculated properties can be plotted versus time, temperature, or frequency, as well as versus any other calculated property using DEA Standard Data Analysis Software.
Applications

Much valuable information about the molecular and rheological behavior of materials can be obtained through dielectric analysis. Quantitative, reproducible data generated by the TA Instruments DEA helps scientists identify the chemical structure of materials and predict processing behavior and end-use performance.

Specifically, the DEA can characterize molecular relaxations, monitor the flow and cure of resins, and calculate activation energies for molecular relaxations. DEA’s ultrasensitivity makes possible the detection of transitions which are not seen by other techniques. Ability to measure bulk or surface properties of materials in solid, paste, or liquid form makes the DEA exceptionally versatile and useful.

Sensor selection depends on both the physical form of the material being examined and the objectives of the experiment. The single-surface sensor is designed for evaluating surface properties. It is ideal for monitoring the cure of liquid or low-viscosity resins that can flow enough to fill the spaces between the sensor’s interdigitated electrodes. Parallel-plate sensors, designed primarily for evaluating bulk properties, are ideal for use with solid materials. Their use can be extended into the liquid region by taking advantage of the DEA 2970’s ability to control and monitor sample thickness and applied force.

The following examples are representative of the broad capability and utility of the TA Instruments DEA 2970.

Molecular Relaxation Studies

Transitions in PMMA

The high sensitivity of the DEA 2970 makes it ideal for characterizing molecular relaxations, which are key predictors of the end-use performance of many polymer products. With its exceptionally wide frequency range, covering eight decades, the DEA 2970 can easily separate multiple transitions, as demonstrated in Figures 16 and 17. These multifrequency curves show that the α and β transitions become increasingly distinct as the test frequency is decreased; they start to become discernible at about 1kHz, and are well defined at 100Hz.

The α transition, which involves motion in long segments of the main polymer chain, is related to the glass transition temperature. The β transition involves rotation of short-chain ester side groups and therefore occurs below Tg. The frequency dependency of the β transition temperature can be used to calculate activation energy for the molecular motion, which provides important information for characterizing the structure and predicting the performance of polymeric materials. In this dielectric analysis experiment, the calculated activation energy for the β transition in PMMA is 17.7 kcal/mole. This correlates well with the values calculated from dynamic mechanical and creep experiments.
Influence of Beta-Alkyl Substitution in Polymethacrylates

The changes that occur as a result of the beta-alkyl substitution of polymethacrylates can be easily observed using dielectric analysis. Figure 18 shows the loss factor data for polymethyl methacrylate (PMMA), polyethyl methacrylate (PEMA), and polybutyl methacrylate (PBMA) at a constant frequency of 3Hz. This figure clearly shows the changes that occur for the polymer as the size of the non-polar alkyl group increases; the alpha transition significantly decreases in temperature, while the beta relaxation remains essentially constant with respect to temperature, but decreases in magnitude. The beta transition is merged with the alpha transition for PBMA.

Analysis of Thin Film Polymers

An important experimental consideration for thin film (∼1.25 mm) analysis is the quality of the contact between the sample and the measurement electrodes. One way to improve contact and eliminate the effects of interfering gas molecules is to sputter coat the sample surface under vacuum with a conducting layer of metal ions (usually gold). The area of the sputter coating is controlled to a known geometry using an overlay mask. When the sample is used in conjunction with the sputter coated (thin film) electrodes, excellent results are achieved.

Figures 19 and 20 show the DEA results for a 31 micron sample of polysulfone film evaluated after sputter coating. The transition seen in both curves is the alpha transition (Tg) which reflects the large-scale microbrownian motion in the amorphous phase. The Tg is observed as a step change in the permittivity and as a peak in the 1Hz loss factor curve at about 180°C. Polysulfone yields an ambient temperature permittivity (3.0) at 1kHz which is in excellent agreement with the expected value of 3.14.

The use of the sputter coated sensors also permits the analysis of polymer coatings on metal substrates.

Compositional Analysis of EVA

Dielectric analysis is an effective tool for characterizing the differences in polymers with respect to composition, blend formulation, thermal history, and moisture content.

Figure 21 shows a comparison plot of the dielectric results obtained at 1kHz from a series of ethylene vinyl acetate (EVA) copolymers containing different levels of vinyl acetate (14, 18, 25, 28, and 33%). These loss factor curves show that the glass transition (Tg) temperature is relatively insensitive to the level of vinyl acetate. However, the intensity of the loss factor peak at the Tg is very dependent on the vinyl acetate concentration. As the level of vinyl acetate increases, the magnitude of the loss factor peak increases. This is consistent with the fact that increasing the level of vinyl acetate increases the flexibility of the polymer. These results indicate that a DEA analysis based on calibration with a series of known EVA formulations could be used to follow vinyl acetate content.
**Cure Studies**

*Rheological Changes in an Urethane*

DEA can characterize dramatic rheological changes in resins before, during, and after cure. This information can be used to identify the appropriate storage temperature and processing conditions for thermosets, elastomers, adhesives, coatings, and many other polymeric materials.

The curves in Figures 22 and 23 show such rheological changes for an uncured and partially cured urethane-isocyanate mixture respectively. This very viscous mixture is applied to a ceramic single surface sensor with a spatula. The sensor and samples are then placed in the furnace, cooled to -75°C, and heated at 3°C/minute. The curves describe the effect on the material. The glass transition event of the uncured resin occurs at a temperature of approximately -60°C as reflected by the frequency dependent peaks in the conductivity curves. As the resin is heated from -60°C through Tg to about 0°C, the viscosity decreases, as indicated by the increase in the conductivity, which is due to the increased mobility of free ions. At 60°C, the free ions achieve their maximum mobility. At this point, volatilization begins and the conductivity curves show a decrease. Above 100°C a more pronounced decrease is observed in the conductivity as the temperature-induced fluidity is overshadowed by an increase in molecular weight and network formation restricting ionic mobility. The cure is complete at about 150°C.

Upon reheating the cured material, the glass transition of the cured resin system has increased to 20°C as reflected by the conductivity curves.

Curing studies such as this can be combined with isothermal experiments to generate time-temperature-transformation diagrams for a material. The resulting information is critical for optimizing storage, shipping, and processing conditions.

**Vitrification in an Epoxy/Amine**

Vitrification is the process by which chemical reaction is quenched during the curing cycle. It prevents a resin from achieving a fully cured state. This is of critical concern because full cure is often required for optimum end-use properties such as mechanical strength and solvent resistance, while incomplete cure can be a desirable means of sustaining impact resistance.

Dielectric analysis is a sensitive technique for monitoring vitrification as shown in figure 24 for an epoxy/amine material. This evaluation was performed at an isothermal temperature of 170°C and a single frequency (10kHz). Initially, the resin flows and its viscosity decreases as the material reaches temperature. After several minutes, however, cure begins and the ε" value decreases. Eventually the Tg advances to a temperature which exceeds the experimental isothermal temperature, the material becomes more brittle and less rubbery, and a peak occurs in the ε" curve reflecting vitrification. DEA curves such as this facilitate choice of processing conditions which control the level of vitrification.
Thermal History Studies
Flow and Cure of an Aerospace Adhesive

The rheological changes in a material during complex thermal histories can provide valuable information about processing, chemical structure, and end-use performance. The DEA 2970, unlike standard parallel-plate rheometers, can characterize dramatic and rapid changes in a polymer’s physical state, even into the final stages of cure, which can significantly influence the physical and chemical properties of the finished product.

Figures 25 and 26 describe the flow and cure of a B-staged aerospace adhesive during a complex thermal history, using parallel plate sensors. Specifically, Figure 25 shows how the loss factor (log $\varepsilon^\prime$) changes with time and temperature. The increase in log $\varepsilon^\prime$ between 25°C and 80°C is due to softening of the adhesive. As the temperature is held isothermally at 80°C for 30 minutes, log $\varepsilon^\prime$ remains constant. Then, between 60 and 75 minutes as heat is applied at a rate of 1°C/min, temperature-induced fluidity causes the viscosity of the resin to decrease. After 75 minutes, the resin polymerizes and develops a three-dimensional network, as indicated by the decrease in log $\varepsilon^\prime$.

Figure 26 is a plot of a log conductivity (pmho/cm) against time for the same thermal profile. That portion of the time/temperature schedule in which log conductivity curves are independent of the test frequency shows that the loss factor measurement (Figure 25) is dominated by ionic movement (or DC conductivity). Those regions of the curve in which the value for log conductivity displays a frequency-dependency indicate that the measurement is strongly influenced by dipole relaxations. The log conductivity curves are frequency-dependent between 0 and 20 minutes because the B-staged resin passes through its glass transition region as it is heated. Between 85 and 160 minutes, the conductivity curves are frequency-dependent because dipole molecular relaxations dominate the measurement as the resin reads and develops molecular weight.

By comparing log conductivity profiles with loss factor measurements, the operator can identify the window in the process during which the material is fluid (and therefore workable), develops molecular weight and cross-links (which is critical to product performance and appearance), and is completely cured (which identifies the proper time to demold the product or remove jigs). The DEA also can record the dielectric properties of the resin during cooling.

Through off-line product development, the scientist or engineer can use DEA to optimize the processing thermal history of products, and predict material processibility and end-use product performance.
Specifications

Temperature Range:
Ceramic Parallel Plate: -150°C to 500°C
Ceramic Single Surface: -150°C to 500°C
Ceramic Thin Film: -150°C to 500°C
Remote Single Surface: -100°C to 250°C

Temperature Control:
Optimum Heating Rate: 0.01 to 5°C/min
Maximum Heating Rate: 50°C/min (over limited heating range)
Cooling (with LNCA): 0.01 to 10°C/min (down to ambient)
: 0.01 to 5°C/min (down to -150°C)
Isothermal Stability: ± 0.2°C

Sample Dimensions:

<table>
<thead>
<tr>
<th></th>
<th>Ceramic Parallel Plate</th>
<th>Ceramic Thin Film</th>
<th>Ceramic Single Surface</th>
<th>Remote Single Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>25 mm</td>
<td>25 mm</td>
<td>20 mm</td>
<td>3.8 mm</td>
</tr>
<tr>
<td>Width</td>
<td>25 mm</td>
<td>25 mm</td>
<td>25 mm</td>
<td>2.5 mm</td>
</tr>
<tr>
<td>Minimum Thickness</td>
<td>120 μm</td>
<td>10 μm</td>
<td>125 μm</td>
<td>12.5 μm</td>
</tr>
<tr>
<td>Maximum Thickness</td>
<td>2.5 mm</td>
<td>2.5 mm</td>
<td>6.0 mm</td>
<td>No Limit</td>
</tr>
</tbody>
</table>

Frequency Range: 0.003 Hz to 100 kHz
Maximum Number of Frequencies Scanned per Experiment: 28
Applied Voltage: 1 Volt (peak)
Measured Amplitude Precision: 0.1%
*Phase Angle Accuracy: 10⁻⁴ Radians
*Tan δ Sensitivity: 1 x 10⁻⁸
*Dielectric Constant Sensitivity: 0.01
Dielectric Constant Range: 1 to 10⁻⁴
Dielectric Constant Precision (Parallel Plate at 25°C): ± 5%
Loss Factor Range: 0 to 10⁻⁸
Conductivity Range: 10⁻⁸ to 10⁻¹⁸ pmhos/cm
Force Setting Range: 5 to 500 Newtons

* Measured at 1kHz and 25°C with 10 second sampling period:

TA Instruments Commitment

The DEA 2970 Dielectric Analyzer is designed and engineered to assure easy, reliable, trouble-free operation. It is supported by a full range of services, including an applications laboratory, publications, training courses, seminars, and a telephone Hotline for customer consultation. Highly qualified service personnel, specialized in thermal analyzer maintenance and service, are available throughout the world. All of those items reflect TA Instruments commitment to providing thermal analysis products and related support services that deliver maximum value for your investment.