TA Instruments recently made several organizational changes designed to strengthen our ability to serve customers in Europe. These changes include formation of a direct office in Spain, addition of Technical Representatives in France and Germany, addition of a Service Specialist in BENELUX, and formation of an applications/service support team for increased collaboration with our distributors in the Scandinavian and Mediterranean countries as well as the Middle East.

TA Instruments is proud to announce the formation of a new direct office in Madrid to cover the thermal analysis and rheology markets in Spain.

This new office will be responsible for all sales, applications, service and commercial issues associated with thermal analysis and rheology. José Miguel Benlloch, who has experience representing TA Instruments products while working for our previous Spanish distributor, has joined TA Instruments as a permanent employee and will head this office. The Madrid office will house a fully equipped demonstration and applications laboratory. The contact information is:

TA Instruments
Avenida Europe 21
Planta Baja
28100 Alcobendas
Madrid, Spain
Phone: 34(9)16618448
Fax: 34(9)16610655

(Continued on page 8)
S. Aubuchon

Since its introduction nearly five years ago, Modulated DSC (MDSC™) has demonstrated several unique applications relating to polymer characterization including:

- Separation of complex transitions into more easily interpreted components
- Increased sensitivity for detection of weak transitions
- Direct measurement of heat flow & heat capacity changes from a single experiment.

Although less familiar, many of these benefits also apply to food science, since many of the transitions in those materials are similar to the transitions observed in polymers. This paper illustrates some typical examples where MDSC is used to characterize foods.

Processing & Storage of Frozen Solutions

Researchers in food science are interested in ensuring long-term stability (shelf-life) of frozen food systems. Ideally, those products should be stored at temperatures below their glass transition temperature (Tg) so that they retain their physical and chemical properties for extended periods. Thus, the foods scientist is interested in determining the influence of freezing, storage and food composition on this transition.

Foods are complex mixtures of materials, typically consisting of carbohydrates, proteins, fats and water. Each of these constituents can display unique thermal behavior, as well as varying interaction with each of the others. For example, carbohydrate sugars are water-soluble, whereas cell wall polymers may merely be plasticized or softened by water. Hence, the Tg of these materials is often difficult to measure by standard DSC because the heat capacity change at Tg is small and overshadowed by other larger transitions. MDSC, on the other hand, can detect these weak Tg’s because of the technique’s increased sensitivity and ability to separate overlapping transitions.

Amorphous structures in sucrose solutions are usually formed by some process condition, such as freeze-drying or freeze-concentration. Freeze-concentration of foods typically results in the formation of a phase which contains amorphous solids and associated unfrozen water. As the temperature is lowered further, kinetic restrictions cause ice formation to cease. The associated or “trapped” water plasticizes the sucrose, lowering the Tg to sub-ambient temperatures observable by MDSC. When these solutions are heated through the Tg, the trapped water is liberated from the amorphous phase. The glass transition occurs simultaneously with the crystallization of the “freed” water. By standard DSC, these two transitions overlap and make interpretation difficult.

Figure 1 shows the MDSC experiment of a 40% w/w sucrose/water solution processed by rapidly quenching from ambient to -60°C. MDSC separates the exothermic crystallization (seen in the nonreversing heat flow) from the glass transition (observed in the reversing heat flow), thus allowing more accurate Tg assessment. This result is consistent with the phase diagram for sucrose published by Roos, et al (Figure 2). In this diagram, an area of maximum ice formation is seen at temperatures between the Tg and the onset of melting. An identical solution cooled at 1°C/min does not exhibit this crystallization process on subsequent reheating. Nearly all crystallization is accomplished upon slow cooling of the sample, and no water is bound into the amorphous phase (Figure 3). The large step change in the Reversing Heat Flow signal at -35°C is believed to be due to the onset of melting, not the Tg.

The formation of ice crystals at the Tg is further resolved by stepwise quasi-isothermal MDSC. In this experiment, the heat capacity of the amorphous sucrose during the Tg is recorded over narrow temperature increments. In the quenched sample, the Cp during the Tg continues to decrease at isothermal temperatures (Figure 4). This is visually indicated by the vertical lines rather than the dots in Figure 4. This indicates latent heat evolution consistent with a kinetic process such as crystallization of water. The solution cooled at -1°C/min shows stable Cp values in this region. Since more perfect crystals are formed on slow-cooling, there is no
water bound into the glassy phase, and no crystallization is taking place on subsequent reheating.

**Crispness of Snack Foods**

Crispness is often a measure of freshness in the food industry. In order to ensure crispness, the fresh snack must have a self-supporting structural framework of an inherently brittle nature. This can be achieved through intentional manipulation of sample morphology and/or composition to affect the temperature of the glass transition such that it remains well above room temperature. Thus, when consumed, the snack will be in a glassy or brittle state. Alternatively, if the snack is affected by its storage environment such that its Tg is lowered below ambient temperature, the snack will be leathery or rubbery, *i.e.*, stale.

A chocolate cookie was examined by MDSC in two states - directly from the package (fresh), and after overnight exposure under ambient atmosphere (aging). TGA comparison of the two samples (Figure 5) indicates that the aged sample has absorbed components (probably water or adsorbed gases) which constitute about 5% of its total mass. Being composed of numerous ingredients, the standard DSC (Figure 6) of the cookie is somewhat complicated, containing multiple endothermic peaks and step changes. Modulated DSC, on the other hand, resolves the glass transition of the cookie into the heat capacity signal, and thus clarifies the effect of aging upon the sample (Figure 7). In cooling the onset of the glass transition in the fresh cookie is seen at about 60°C, well above ambient temperature. Thus, this cookie would be consumed in the glassy or brittle (“fresh”) region. The Tg of the aged cookie has shifted lower in temperature to about 10°C, most likely due to the plasticizing effect of the adsorbed moisture. This shift results in consumption to be above the glass transition, in the rubbery (“stale”) region. Modulated DSC has separated the complex DSC scan into easily interpreted signals which clarifies the effect of moisture on the inherent structure of the cookie material.

**Protein Denaturation**

Protein denaturation is a process catalyzed by heat, light or other stimuli which causes a dramatic change in the structural conformation of proteins. This order-disorder transition is commonly characterized with DSC by measuring the resulting endotherm which reflects the energy needed to break interactions which stabilize the native quaternary structure. However, with time some degree of ordering redevelops. The magnitude of structure reformed can be evaluated by analyzing the same sample again after storage and comparing the denaturation endotherms.

Figure 8 shows the MDSC results for a thermochemically denatured collagen (or gelatin). The energy required to destroy its structure appears in the non-reversing heat flow and thus provides an indication of structure regained since the time of initial denaturation. An endothermic shift, seen in the reversing heat flow, indicates an increase in heat capacity. Heat capacity is related to molecular motion, *i.e.*, the more available motion, the higher the Cp. The denaturation process results in the breakdown of the quaternary structure leading to increased entropy and motion within the molecule. In turn, this causes an increase in the Cp of the molecule. The quantitative shift in Cp is directly proportional to the amount of structure regained upon storage.

---

For additional information on MDSC of freeze-dried material, see “Freeze-Drying of Liposomes: The Preservation of Liposomes During the Freeze-Drying Process and Their Stability in the Freeze-Dried State”, E. van Winden, Ph.D. Thesis, Utrecht University, The Netherlands.

Acknowledgment: The consultation of Prof. Yrjo Roos, University of Helsinki, Finland contributed greatly to this article and is gratefully acknowledged.

---

The Rheolyst AR 1000 was exhibited for the first time in the U.S. at the 68th Annual Society of Rheology (SOR) meeting in Galveston, TX in February. This year’s meeting and associated exhibit were a success with 300 rheologists in attendance. TA Instruments was proud to be able to contribute to the Society, by sponsoring the “Welcoming Reception” on Sunday evening.

At the Society Banquet on Tuesday evening, the 1996 Journal of Rheology Publications Award, sponsored by TA Instruments, was presented to Dr. Charles Zukowski, for the paper, “Rheological Consequences of Microstructural Transitions in Colloidal Crystals”, L.B. Chen, B.J. Ackerson, and C.F. Zukowski († University of Illinois and ‡ University of Oklahoma State University). Congratulations to the award recipients, and thanks to the SOR board and the local arrangements chairman, Dr. Bill VanArsdale, for a well organized meeting.

Over the past several years, a number of ASTM Committees have explored a wide variety of experimental parameters affecting oxidative induction time (OIT) measurements by DSC in an attempt to understand and improve intra- and interlaboratory precision. These studies have identified test temperature precision as a key parameter affecting OIT precision. Other parameters of importance are oxygen flow rate, specimen size, specimen pan type, oxygen pressure, and catalyst effects. A paper by Blaine, Lundgren and Harris which details these studies is now available in preprint form. Request publication TA 235.

A related paper describing a new proposed polyethylene OIT reference material is also available. Request publication TA 233. Contact Maureen McCord at (302) 427-4111 for copies.

**TMA Quartz Wafers**

Thermomechanical Analysis (TMA) is routinely used to study dimensional changes in materials providing valuable information such as the coefficient of thermal expansion, glass transition temperature, and softening point. However, when some materials are heated above their glass transition or melting point, molten sample can adhere to the TMA quartz stage and/or probe causing clean-up problems. More importantly, when the sample causes the stage and probe to stick together, removal of the applied force at the end of an experiment can sometimes cause breakage of these parts. New quartz wafers are available (PN 944341-901) which cover the quartz stage and eliminate this latter problem.
DSC, TGA AND TMA CERTIFIED CALIBRATION STANDARDS AVAILABLE

The results in most thermal analysis experiments are plotted as a function of sample temperature. Hence, it is important to have a thermocouple located near the sample to accurately track sample temperature. In addition, it is important that this thermocouple be calibrated to compensate for heating rate and purge gas effects. Standard procedures exist for calibrating DSC, TGA and TMA systems. The DSC and TMA procedures are based on the melting points of high purity metals, while the TGA procedure is based on the Curie Point of metals or alloys.

With the growing interest in ISO9000 compliance and similar quality-related initiatives, there is a need for traceable standards for use in these calibration procedures. Hence TA Instruments supplies Calibration Kits to meet this need. (These kits can be used to calibrate thermal analysis systems from any supplier.) The DSC Calibration Kit (PN 915060.901) consists of a primary indium reference material; ASTM E967 and E968 test methods describing the calibration protocol; and the associated ISO9000 documentation, providing both temperature and enthalpic calibration traceability. The TGA Calibration Kit (PN 952384.901) consists of two secondary curie temperature reference materials (alumel and nickel); a suitable magnet; ASTM E1582 test method describing the calibration protocol; and ISO 9000 documentation. The TMA Calibration Kit (PN 944206.901) consists of a primary indium reference material; test method ASTM E1363 describing the calibration procedure; and ISO 9000 documentation. The reference materials used in these kits are traceable to a National Reference Laboratory (NRL).

Contact your local TA Instruments Service Representative for further details.

LEN THOMAS NAMED NEW PRESIDENT OF TA INSTRUMENTS

Effective February 15, Dr. David Chalmers retired as President of TA Instruments. Dave joined TA Instruments in 1973 when the company was still a business unit within DuPont and became Manager of the Thermal Analyzer Business in 1982. Under his leadership, TA Instruments subsequently separated from DuPont becoming the world’s leading supplier of thermal analyzers, expanded into rheology with the acquisition of Carri-Med in 1993, and most recently joined Waters Corporation.

Len Thomas has been named the new president. Len joined the DuPont thermal analysis business in 1975 and held positions in technical sales, market development, product development, sales and business management and most recently, worldwide marketing. Prior to 1975, he was a research chemist in the DuPont Photo Products Department.

Len will continue to focus TA Instruments on satisfying customer needs for innovative technology and superior support.

NEW APPLICATIONS LITERATURE

Summarized below are titles for recent additions to our applications literature list. Contact your local TA Instruments Representative to obtain a free copy of these items.

**Thermal Analysis**

- Modulated DSC Compendium [Ref. No. TA210]
- Characterization of Melting Phenomena in Linear Low Density Polyethylene by Modulated DSC [Ref. No. TA227]
- Optimization of Lyophilization (Freeze-drying) using Dielectric Analysis [Ref. No. TA217]
- Comparison of Thermal Analysis, Rheology, and GPC Results for Modified Polypropylenes [Ref. No. TA218]
- Isothermal Cure and Vitrification of Thermosetting Systems by Modulated DSC [Ref. No. TA219]
- Coating Characterization by Thermal Analysis [Ref. No. TA220]
- Oxidative Induction Time [Ref. No. TA235]
- Determination of Oil in Rubber by Vacuum TGA [Ref. No. TS33]

**Rheology**

- Rheolyst AR 1000 Rheometer Brochure [Ref. No. RH16]
- Selecting Lithographic Inks [Ref. No. RS32]
- Comparison of Commercial Viscosity Modifiers [Ref. No. RS33]
- Rheology Software Models (Flow) [Ref. No. RA9]
- Parallel Superposition Rheology of Thickened Latex [Ref. No. RH060]
DMA Modulus Measurement

J. Foreman

Dynamic mechanical analysis (DMA) measures the modulus (normalized stiffness) and damping (energy dissipation) of viscoelastic materials as those materials are subjected to oscillatory stresses (forces) and resultant strains (displacements). Modern DMS's like the TA Instruments DMA 2980 can evaluate modulus for a wide variety of materials ranging from rigid composites to very weak gels. The nominal modulus range covered by the DMA 2980 is $10^3$ to $3 	imes 10^{13}$ Pascals. The actual range covered for a specific material will depend, however, on four factors. These include the deformational force generated by the DMA drive motor, the inherent stiffness of the DMA drive shaft and sample clamp, the mode of deformation being used, and the geometry (dimensions) of the sample material. Figure 1 shows a schematic of the DMA 2980 which highlights the first three of these factors.

The DMA 2980 uses a non-contact direct drive motor to provide the oscillatory force which deforms the sample material. The motor is built from high performance composites and other materials and is thermostated to eliminate heat build-up. As a result, the motor can deliver reproducible forces over a wide dynamic range 1mN to 18 Newtons and can control the deformation amplitudes from 0.5 μm to 10mm.

The inherent stiffness of a DMA design is limited at the low modulus end by the restoring force and friction of the suspension mechanism. The DMA 2980 uses eight air bearings grouped into two sets of four each near the top and bottom of a rectangular air bearing slide of the suspension system. This results in almost frictionless movement and no restoring force compared to the flexural spring suspension used in conventional DMS's. Hence, very low modulus materials can be characterized with high precision and low noise.

The upper end of a DMS's inherent stiffness range is limited by the drive mechanism as well as compliance (yielding) in the sample clamps. The DMA 2980 clamps are designed with internal I-beam construction based on finite element analysis modeling (Figure 2) to minimize compliance and simultaneously minimize mass (for faster thermal equilibration).

Deformation Modes & Sample Sizes:

- **3-Point Bend**: 5, 10, 15, 20 and 50mm lengths, width to 15mm, thickness to 7mm
- **Single Cantilever**: 4, 10, and 17.5mm lengths, width to 15mm, thickness to 5mm
- **Dual Cantilever**: 8, 20 and 35mm lengths, width to 15mm, thickness to 5mm
- **Shear Sandwich**: 10mm square, to maximum of 4mm thickness each side
- **Tension**: 5 to 30mm length, width to 8mm, thickness to 2mm
- **Compression**: Parallel plates, 15 and 40mm diameter

The most important factors governing the DMA measurable modulus range are deformation mode and sample geometry factor. The DMA 2980 provides all the common modes of deformation including bending (single/dual cantilever, three-point bend), compression, shear and tension. In each mode, modulus is calculated from the experimental data using a specific geometry factor. The geometry factor for the tension mode, for example, is $L/A$ where $L$ is sample length and $A$ is cross-sectional area. The DMA 2980 is unique because it allows modulus to be determined using geometry factors which reflect a variety of well-defined sample shapes (rectangles, solid cylinders, hollow tubes and fibers) and dimensions (Figure 3), or using geometry factors which allow “real-world” shapes like elastomeric windshield wiper blades to be evaluated without extensive sample preparation.

The combination of all these design factors can be represented graphically for each deformation mode. Figure 4 shows such a plot for the dual cantilever clamps. The area enclosed by the solid line represents all possible combinations of sample modulus and size for which the dual cantilever clamps are suitable. This graphical format facilitates selection of the appropriate deformation mode, and sample size based on expected modulus range. For example: if over the temperature range of interest, a material’s modulus was expected to vary between 10GPa ($10^{10}$ Pa) and 1MPa ($10^6$ Pa), and we wanted to use the dual cantilever mode, then we would need to select a sample size with a geometry factor in the range of $10^6$ to $10^3$, as represented by the area enclosed by the dashed line.

To learn more about DMA modulus measurement and tips on selecting measurement modes and sample dimensions, request publication TA-234.
Evaluation of Powder Coatings

D. Chaney

Powder coatings are thermoset materials widely used in products like household appliances. During processing, these materials are “fusion-bonded” (cured) to cover and protect metal surfaces. To ensure appropriate processing, parameters such as the glass transition, gel point, heat of cure and cure kinetics must be known. Both differential scanning calorimetry (DSC) and rheology can be used to provide this information.

Figure 1, for example, shows the DSC curve for an epoxy powder coating. Two transitions are observed, 1) a glass transition at 57°C where the coating softens sufficiently to flow, covering the surface, and 2) a cure exotherm beginning at 96°C where the coating actually bonds to the surface. In this case, the glass transition is accompanied by a large endothermic relaxation peak associated with previous storage/processing of the material. The glass transition can be estimated using its onset temperature provided the operator does not misinterpret this event as a melt. (Note, the application of MDSC® would clearly separate the Tg from the corresponding endotherm relaxation.) Immediately above the Tg and relaxation, this epoxy begins to cure. The temperature associated with the onset of cure (97°C), the temperature of maximum cure rate (153°C), and the total heat associated with cure (59.4 J/g) obtained during constant heating (in this case at 10°C/minute) are not only useful in quickly comparing similar formulations, but more importantly can also be used to project processing time under different isothermal conditions. In this case, the epoxy follows nth order kinetics (dα/dt = k(T)(1-α)^n), and hence a Borchardt & Daniels treatment readily yields the isocconversion curves such as those shown in Figure 2. Plots like this indicate how much time is required at a specific processing temperature to obtain the desired level of conversion (cure).

If a thermoset powder coating is cooled after the initial heating experiment shown in Figure 1 and then reheated, the properties, particularly the new glass transition temperature, of the fully cured material can be obtained. Figure 3 shows these comparative first and second heating results for a powder coating where the two materials were evaluated simultaneously in a dual sample DSC. As expected, the second heat material has a higher Tg and no residual curing exotherm. The dual sample DSC assures that the experimental parameters (e.g., purge gas) are consistent and hence are eliminated as potential causes for the differences observed.

Rheology, which is an analytical technique that measures the deformation and flow of materials, provides an additional piece of information on powder coatings. Figure 4 shows the oscillation results for a polyester powder coating. In oscillation, the amplitudes of an applied stress and resultant strain, as well as the phase angle between the two, are used to determine the relative amounts of elastic (storage modulus G’) and viscous (loss modulus G”) behavior in the material. For thermosets, the point at which G’ = G” (i.e., tan delta = G”/G’ = 1) is generally considered to be the gel point (i.e., the point at which structure formation starts). In this example, the gel temperature is 190°C. The results from three separate evaluations are shown to illustrate the reproducibility possible.

More information about the use of DSC and rheology, as well as DMA, TMA, and DEA, in characterizing thermosets can be found in TA Instruments Publications TA219, TA126, TS11, RS24 and RS29.
The formation of this office will enable us to provide our customers in Spain with the same high level of customer service and support that have become synonymous with the name TA Instruments.

Continued growth and expansion of our French office is evidenced by the addition of Carole Rossinelli and Frédéric Jupin. Carole joins TA Instruments as a Rheology Sales Engineer for France. She is a graduate of the University of Strasbourg with a degree in Polymer Chemistry. Frederic joins TA Instruments as a Sales Engineer with responsibility for Thermal Analysis and Rheology products in Northern France and in the French speaking part of Belgium. Frederic is a graduate of the University of Paris VI with a degree in Polymer Chemistry.

A European Distributor Support Team has been formed to provide an increased level of support to our distributors in Scandinavian, and Mediterranean countries as well as the Middle East. This new support team will give our distributors direct access to the necessary experts and increase their ability to serve customers.

TA Instruments is committed to providing the highest level of customer support and service to our customers throughout Europe and around the world. Stay tuned for continuing developments.

New Thermal Analysis Textbook Available

The Second Edition of Thermal Characterization of Polymeric Materials, edited by Edith A. Turi, is now available. It provides an in-depth overview of thermal analysis by focusing on instrumentation and a wide array of applications in research, development, production, quality control and technical service.


Thermal Characterization of Polymeric Materials
Edited by Edith A. Turi (Polytechnic University, Brooklyn, NY)
For your convenience, the book is available from TA Instruments, order as P/N 299900.001

Visit the TA Instruments Web Site

Now in its second year, the TA Instruments home page offers an additional method by which you may contact us. The home page provides a product listing, complete with descriptions as well as literature request forms, allowing us to provide you with the information you need as quickly as possible. Displayed on-line is a selection of applications literature featuring background theory and functionality of popular techniques and equipment.

http://www.tainst.com

Also included is a current list of TA Instruments agents and distributors around the world. Links are provided to other sites of interest such as the Journal of Rheology, the American Chemical Society and the Society of Plastic Engineers. Check for regular updates in the “whats new” section.