THE TA HOTLINE

Modulated TGA™
Introduced at 1997 NATAS Conference

TA Instruments proudly introduced a new technique, Modulated TGA™ (MTGA™) at this year’s NATAS (North American Thermal Analysis Society) conference in September.

This patent pending technique is the result of TA Instruments’ continuing research and development in the area of variable heating rate thermal analysis. MTGA is the third technique (patented techniques Hi-Res TGA™ & MDSC® are 1st and 2nd) to apply variable heating rate technology. MTGA is based on TGA kinetics work pioneered by Dr. Joseph Flynn of NBS.

Modulated TGA delivers simultaneous weight loss and kinetic analysis without the time and single decomposition mechanism limitations of the traditional technique. MTGA, like its predecessor MDSC, superimposes a sinusoidal temperature modulation on the traditional linear heating profile.

Just as it does in MDSC, the application of a sinusoidal temperature program produces a change in the response of the test specimen. In MTGA it is the rate of weight loss that responds to the temperature oscillations. The measurement of the rate of weight loss provides an experimental tool to study the kinetics of decomposition or volatile reactions. The use of discrete fourier transformation allows kinetic parameters such as activation energy and pre-exponential factor to be calculated on a continuous basis. This permits the study of decomposition kinetics as a function of other experimental parameters such as time, temperature, and conversion.

Advantages of Modulated TGA include:
- Model-free calculation of Activation Energy
- Calculation of Pre-exponential Factor with 1st order assumption
- Continuous measurement of Activation Energy and Pre-exponential Factor
- Increased productivity

There was substantial interest in MTGA at the NATAS conference, and development continues as we work to fully understand the capabilities and applications of this exciting new technique. For additional information request TA publication number TA-237 or contact your local technical representative.

Rheology Navigator 2 & 2plus released

This much anticipated upgrade to our popular rheometer software began shipping as of October. Rheology Navigator 2 is a 32-bit multitasking program for the Windows® 95 operating system. Continuing the tradition of its predecessor, versions 2 and 2plus have further enhanced capabilities and easier operation. They provide powerful direct control of a rheometer with full automation of data generation and analysis.

UNCOMPLICATED SCRIPT DEVELOPMENT

The use of scripts can automate all rheometer functions and may be used to run a method repeatedly with the operator needing only to change samples at prompted intervals. Long or complex experiments may be run unattended and you have the option of creating a library of scripts for distribution thereby assuring the integrity of results performed at many locations by operators of varying experience.

The new “record” mode allows a script to be automatically generated in the background during normal rheometer operation. For manual script development the editor prompts the correct use of statements and syntax. A toolkit of basic

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A Subsidiary of Waters Corporation
Edith Turi honored at PittCon

Dr. Edith Turi, was recognized by TA Instruments for her contribution to the science of Thermal Analysis, and for her dedication to promoting its understanding and application. Dr. Turi is course director for the American Chemical Society (ACS) short course, Thermal Analysis in Polymer Characterization. This intensive program offers guidance for applying thermal analytical methods to polymer research and production.

Attendees at the course preceding PittCon this year, marked the 1000th student to attend Dr. Turi’s course, and to benefit from her technical guidance and personal attention. No other ACS Short Course has achieved this level of participation.

TA Instruments applauds this achievement as just one of the many ways Dr. Turi has contributed to the education of thermal analysts around the world.

Melting Phenomena by MDSC®

Because of its ability to separate “total” heat flow into its heat capacity and kinetic components, Modulated DSC™ provides unique insights into polymer melting and related phenomena, including:

- separation of simultaneous crystallization and melting processes
- more accurate measurement of the temperature range of melting
- increased precision of heat capacity measurements
- more accurate measurement of the initial crystallinity of polymers

The study of the melting of polymers is probably the most common use of DSC. However, the application of MDSC® to the melting region is often misunderstood. Adherence to a few simple experimental guidelines enables us to easily apply MDSC to the melting transition, providing an increased understanding of this event. MDSC parameters optimized for analysis of the melting region are as follows:

Modulation Period

A period between 40 to 100 seconds should be selected when using helium as a purge gas, and 60 to 100 seconds with a nitrogen purge.

Underlying Heating Rate

A heating rate which provides a minimum of 4-5 cycles at the half-height of the sharpest melting peak should be selected.

Modulation Amplitude

An amplitude which provides cyclic heating only (no cooling) and causes the heating rate to periodically go to 0°C/min should be selected. This is done with the use of the table shown in Figure 1.

The primary reason for having the heating rate periodically go to 0°C/min is to eliminate the contribution of heat capacity to the heat flow signal. When the heating rate goes to zero, the heat capacity contribution to the total heat flow signal also goes to zero and this permits continuous, time-dependent processes such as crystal perfection or crystallization to be observed in the raw, modulated heat flow signal. The heat flow at the lowest heating rate is seen along the top of the modulated heat flow signal. Hence, the top of the modulated heat flow signal should have the same shape as the Nonreversing signal, which is the calculated MDSC signal for time-dependent processes.

For additional information on the application of MDSC to the melting region, request TA publication number TA-227, “Melting Phenomena in Linear Low Density Polyethylene by MDSC®”.

Dr. Wei-Ping Pan receives NATAS Fellowship Award

Dr. Wei-Ping Pan, Sumpter Professor of Chemistry at Western Kentucky University (Bowling Green, KY USA), was named a Fellow of the North American Thermal Analysis Society at the conference this year. The NATAS Fellowship award acknowledges and honors individuals who have records of distinguished scientific achievement, significant technological accomplishment, and/or outstanding scholarship in the field of Thermal Analysis.

Dr. Pan established the Thermal Analysis Laboratory at Western Kentucky in 1986 which, under his direction and leadership, has developed into an internationally recognized facility. He has published over 100 papers and lectured internationally on the subject of Thermal Analysis. Recent accomplishments include his position as Chair of the successful NATAS Short Course. We join Dr. Pan’s other colleagues in congratulating him on this latest award!
Post NATAS MDSC® Seminar an Overwhelming Success!

TA Instruments sponsored a two-day MDSC seminar in McLean, Virginia following the 1997 NATAS® conference. Attendance at the seminar rivaled that of the NATAS conference itself.

The first day of the seminar consisted of presentations by respected scientists from around the world. Speakers and Topics were:

- A Temperature-Modulated DSC study of the melting of Polymers by Professor Bernhard Wunderlich of the University of Tennessee.
- Application of Modulated DSC to crystallization kinetics of polymers: the application of the phase angle in these measurements by Professor Akihiko Toda of the University of Hiroshima.
- The use of MDSC in the pharmaceutical sciences by Prof. Duncan Craig of the London School of Pharmacy.
- New developments in the use of MDSC to study reacting polymer systems by Professor Bruno van Mele of the Free University of Brussels.
- Application of Modulated DSC to the freeze-drying process by Professor Steven Nail of Purdue University.
- Latest developments in calorimetric analysis with scanning microscopy (CASM) and mechanothermal analysis with scanning calorimetry (MASM) by Dr. Michael Reading, inventor of Modulated DSC, Loughborough University of Technology.

The second day featured presentations by Dr. Steve Aubuchon and Len Thomas of TA Instruments providing training designed to help MDSC users gain maximum benefit from their investment. Topics included calibration, selecting optimum conditions, interpretation of results, sources of error and typical applications.

TA Instruments takes seriously our commitment to provide superior customer service and support after the sale. This seminar is an example of that commitment. Attendees were encouraged to complete seminar evaluation surveys, and feedback was very positive with a 98% approval rating. Almost half of the attendees commented that the seminar exceeded their expectations. Comments included:

“TA Instruments has once again done an excellent job in their support of customer training. This seminar was one of the best I have ever attended in my years of scientific endeavors”

Fortune 500 Polymer Scientist

The many MDSC papers and posters presented at the NATAS conference (approx. 20% of all papers/posters presented at NATAS involved MDSC), and the response to this seminar are evidence of the significance that Modulated DSC™ plays in modern thermal analysis. As a scientific community, our understanding and application of MDSC continues to grow, encompassing a wide range of materials and applications.

* NATAS is the North American Thermal Analysis Society. For information on NATAS, contact: The Complete Conference, Inc., 1540 River Park Drive, Suite 111, Sacramento, CA 95815 telephone (916) 922-7032

Improved Applications Library CD-Rom

TA Instruments is recognized as a leader in providing after-the-sale assistance so users receive maximum benefit from their instruments. One of the many ways we provide this support is in the generation and distribution of technical applications literature. In mid 1996, TA Instruments introduced a CD-Rom that included a wide range of applications papers. Positive response has prompted further development resulting in the release of an updated version.

The new Applications Library CD contains many new papers, a total of 210 documents covering a wide range of Thermal Analysis and Rheology applications. Documents are provided in Adobe Acrobat portable document format for easy viewing or printing. All necessary software is included on the CD, and is compatible with Windows 3.1, 95, NT, OS/2, and Mac. The CD is indexed with links allowing easier retrieval, as well as searches by content, author, subject, title or document number. To order the new Applications Library CD, contact your local representative, or call TA Instruments at (302) 427-4000 and ask for Part number 925700-901.

Accessories Price List

The Accessories Parts and Supplies price catalog (US) is now available by calling (302) 427-4000. A convenient reference categorized for ease of use. Includes cost, descriptions and item numbers.

Hotline by e-mail?

Today, many individuals and companies rely on electronic communications because of the associated ease of delivery, organization, storage, and retrieval of information. We have begun to get request from readers interested in receiving the Hotline via e-mail and are looking into the possibility of distribution as an Adobe Acrobat PDF document. (Adobe Acrobat reader software is included on the Applications Library CD, or can be downloaded from the Internet at no charge) If you, or one of your colleagues, are interested in e-mail delivery, please respond to: hotline@tainst.com

Please include your name, affiliation, address, phone, fax, and e-mail address so we can insure accuracy of our records. We will measure the response to determine if this service will be offered.
A successful ISO 9000 audit

The internationally recognized ISO 9000 quality standards were established to assure customers that products and services are provided in a manner that satisfies their needs. ISO prescribes a well documented management system which targets a problem, and quickly corrects the appropriate process, to eliminate it.

TA Instruments led the way in September 1992 by being the 413th (current count exceeds 14,000) business in the United States to receive certification. We are proud of this position but refuse to rest upon its success. We emphasize the importance of each individual employee to constantly strive for improvement with the goal of nothing less than total customer satisfaction. The benefits of this work ethic have shown themselves many times. (See Hotline 1997 volume 1, page 4)

Internal audits are performed regularly by our resident auditor certified by the American Society for Quality. Our most recent annual audit performed by a RAB registrar found the quality system in compliance, as has been the case since initial certification. The receipt of this formal recognition assures us that the necessary safeguards are in place and provides you with the confidence that your investment in TA Instruments products and services will deliver maximum value.

Thermal Analysis Reference source available


The fully revised and updated second edition of this widely acclaimed work continues the tradition of the original book. It provides an in-depth overview of thermal analysis by focusing on instrumentation and a wide array of applications. The well-coordinated chapters, written by world-renowned authors, are replete with practical examples and include important, previously unpublished research. This comprehensive work is an invaluable reference source for chemist, engineers, physicist and other professionals involved in research, development, production, applications, characterization and evaluation of polymers.

Available from TA Instruments, order as P/N 299900.001

Year 2000 Compliance

Much media attention lately has been devoted toward concern for software to properly interpret the addition of another century to their internal time keeping.

The problem originated nearly thirty years ago when programmers began using only two digits to represent the year (97 as opposed to 1997). The fear is a computer's inability to distinguish between the year 2000 or 1900. Your bank's computer for example may suddenly interpret your loan payment as being 100 years past due. All manner of data from pension benefits to prison sentences may be distorted.

Thermal Solutions software, supplied by TA Instruments is in compliance with Year 2000 date guidelines. This quality software supports the date range from 1 January 1980 through 31 December 2079 with stored dates explicitly identifying the century. The software supports all manipulations and computations of time and date, produces the desired results, is seamless in its implementation, and requires no special data handling or manual intervention over the supported range.

Expanded Lab Facilities in Chicago

At our office in Rolling Meadows Illinois, you will see all the instruments in operation and discover what new technologies are available to fill your growing needs. Receive a hands-on evaluation of our equipment and decide for yourself. The office is conveniently located off I-90 between O’Hare airport & the Woodfield Mall. Time is money so invest it wisely. Call today and set up your appointment 302-427-4170.

Organizational Events

TA Japan Relocates

This relocation to a much larger facility with more staff, will increase TA Instruments capabilities in Japan. Our expanded laboratory will be very convenient for customers wishing to see analysis techniques.

TA Instruments Japan KK
No. 5 Koike Building
1-3-12 Kitashinagawa
Shinagawa-Ku, Tokyo 140, Japan
Phone: 81-3-3450-0981

We also have a branch sales office in Osaka to better serve our customers in Western Japan.

Sales Achievement Award

The Shindo Scientific Company Ltd., Seoul Korea was presented with this beautiful lead crystal award for outstanding sales achievement in 1996. Shindo more than doubled forecast sales for the year.
The rheology of a typical cosmetic emulsion looks like Fig 1, showing a yield point, shear thinning behavior, and a time-dependent structure breakdown that results in hysteresis i.e. thixotropy. Viscosity is a strong function of shear rate (Fig 2), i.e. the processes the emulsion is undergoing (Fig 3). As a general rule, if the yield point, infinite [shear around $10^3 \text{ s}^{-1}$] viscosity, and the thixotropy of two emulsions are the same, they will have the same primary skin feel, to the extent that a testing panel cannot tell the difference. Yield point gives the resistance the emulsion offers before flowing. Infinite viscosity characterizes how the emulsion behaves during spreading. Thixotropy gives an indication of the degree to which the emulsion flows into the skin’s valleys. If structure recovery is quick (quasi “solid” behavior), the formulation will remain on the skin’s peaks, giving a greasy feel. If structure recovery is slow (or there is no structure at all, as in a Newtonian fluid), the formulation will disappear into the skin’s valleys, giving a dry feel (Figure 4). At intermediate thixotropies, an even, occlusive film will be formed on the skin. By understanding the relationship between formulation variables and these rheological parameters, any desired primary skin feel can be engineered.

IFAC’s standard thixotropy measurements can be roughly translated as below, but must be interpreted alongside the infinite (1000 1/s) viscosity values: above 200 mPas gives a greasy skin feeling, while below 50 mPas gives a dry skin feeling.

<table>
<thead>
<tr>
<th>Thixotropy values</th>
<th>Film formation on skin</th>
<th>Skin feeling</th>
</tr>
</thead>
<tbody>
<tr>
<td>-20,000 to 0</td>
<td>inhomogeneous</td>
<td>greasy and tacky</td>
</tr>
<tr>
<td>0 to 50,000</td>
<td>homogeneous</td>
<td>acceptable</td>
</tr>
<tr>
<td>50,000 to 200,000</td>
<td>inhomogeneous</td>
<td>dry</td>
</tr>
</tbody>
</table>

**Rheology Navigator Software**

Continued from page 1

rheometer functions and mini-scripts are supplied which may be blended into new scripts. Any script may be run from within another, allowing the incorporation of previously developed methods.

**Navigator 2 Plus** offers the added benefits of a debug mode allowing scripts to be run step by step to resolve errors and ensure correct operation. Also included is the feature of conditional execution. This permits statements to be written that allow the software to make intelligent decisions based upon operator input or the results obtained from a sample. Use of these statements within scripts allows automation of decisions and hence complex methods may be followed automatically.

**Information Library**

The Navigator Compendium included with 2 plus is an expert system that provides the operator with access to a wealth of rheological knowledge. The compendium offers help in choosing the appropriate geometry, test method or interpretation of the data. This may be used to develop rheological knowledge and reduce the learning curve.

“record mode” effortlessly generates a script during normal rheometer operation

Continuing our tradition of excellence in product innovation this upgrade raises a quality product to a higher standard. **Rheology Navigator 2 and 2plus** offer improved ease of operation and more powerful capabilities while retaining the familiarity and reliability you have come to expect from TA Instruments.

To run Rheology Navigator 2 you will need to be using Rheology Solutions software and Windows® 95. For additional information request TA publication number RH-017 or contact your local technical representative.
An MDSC® Study of Heat-Set and Annealing Temperatures

S. Aubuchon

The thermal treatment by which a material is conditioned can affect its processability, storage stability and end-use. In the area of polymeric films and fibers, a process known as "heat-setting" is often used to precondition the material. The heat-setting process involves holding the material isothermally at a particular temperature for a specified time. This process imparts dimensional stability to the material, increases wrinkle resistance, and in the case of fibers, can influence yarn performance.

To this end, thermal analysis has historically been used to monitor the effects of the heat-setting or annealing process. When a polymer is annealed at a temperature between the glass transition (Tg) and melt (Tm), crystalline structure is formed at the annealing temperature. On the second heat by DSC, the degree of crystalline structure can be monitored by investigation of the "middle-endotherm peak" (MEP). This peak appears as a result of heat-setting the material, and may be due to melting of lamellae crystals formed during the heat set process. The position and size of the MEP can help to determine the sample's heat-set history, and can aid in process development and quality control. Figure 1 shows the MEP formed by annealing a sample of poly(ethylether)ketone at 310°C for several hours.

In Figure 1, the MEP appears at a temperature slightly above the heat-set temperature of 310°C, and overlaps the main melting peak of the material.

Modulated DSC™ separates the total heat flow signal (dQ/dt) of standard DSC into two components (equation 1); the heat capacity component (Cpb) and the kinetic component f(T, t). In MDSC, these are referred to as the Reversing Heat Flow and Nonreversing Heat Flow, respectively.

The middle endotherm peak is a kinetically-controlled event, and is well-resolved in the Nonreversing Heat Flow signal, shown in Figure 2.

The ability of MDSC to resolve the middle endotherm peak from overlapping events makes it a useful tool in the analysis of heat-set and annealing temperatures in other polymeric systems.

High-Temperature Thermoplastic

Good quality assurance typically requires constancy in processing. Occasionally, mechanical failures in process equipment can cause molded parts to be subject to elevated temperatures for extended periods of time; thermal events similar to heat-setting. Investigation of the MEPs caused by these thermal events helps to determine the effects on the material.

Figure 3 shows the MDSC of a high-temperature thermoplastic material from a routine molding process. The majority of the melting is resolved in the Reversing Heat Flow signal, whereas the cold crystallization and ongoing crystal perfection up to the bulk melt are resolved in the Nonreversing Heat Flow.

In contrast, Figure 4 shows the MDSC of the same material after a processing abnormality. This sample was held at 300°C for one hour before being cooled. The result was that the material was annealed at this temperature, and the structural morphology was altered. This is apparent in the Nonreversing Heat Flow signal in Figure 4. The cold...
crystallization peak evident in Figure 3 does not appear. In fact, no crystallization takes place below the annealing temperature of 300°C. Holding the sample isothermal has caused the near-complete crystallization of all the material kinetically capable of crystallizing at 300°C. Once the annealing temperature is surpassed, the MEP becomes apparent. This peak is associated with the portion of the material isothermally crystallized at 300°C, and may be the melting of this material. Above the MEP temperature, the crystal perfection process resumes (shaded area), until the bulk melting of the material. The effect of thermal history on this material is relatively easy to interpret from the Nonreversing Heat Flow signal.

**Polymeric Films**

Polymeric films are often heat-treated to impart a specific sample morphology and to maximize performance. The MEP can be used to monitor heat treatment temperature, and within a specific material, heat treatment time at a constant temperature. Figure 5 shows the Nonreversing Heat Flow signals for an HDPE thin film annealed at 110°C for varying amounts of time (30, 60, 120, 240, 480, and 960 min.). As the annealing time is increased, the area of the initial MEP increases, and the subsequent exothermic crystal perfection peak is suppressed. Annealing the material at this temperature crystallizes the sample, which adds area to the MEP, and reduces the amount of less crystalline material available for crystal perfection.

A similar effect is seen in a thin film of PET which was heat-treated in the same fashion. As the bulk melting of PET occurs above 200°C, and the Tg is below 100°C, the sample was annealed at 150°C for the same duration of time. Figure 6 shows a comparison of the Nonreversing Heat Flow curves for the PET sample. As the annealing time increased, the temperature of the onset of the MEP increases, as does the area of the MEP.

A plot of annealing time @ 150°C versus MEP area (Figure 7) illustrates the direct relationship.

**Polymeric Fibers**

PET and other polymers are often spun into fibers for use in fabrics and fillers. These fibers are typically heat-treated to optimize structure and durability. The MEP as detected by MDSC is an excellent indicator as to the specific thermal history experienced by a fiber sample.

Figure 8 shows comparison of the Nonreversing Heat Flow curves for a variety of polyester fibers heat-set at different temperatures. The onset of the MEP indicates the temperature of the heat-setting process. The relative peak area is analogous to the degree of heat-setting. As the heat-set temperature of the fiber is increased, the MEP onset increases in concert. The relative equivalence in peak area suggests that the samples have similar degrees of heat-set structure, applied at varying temperatures.

**Summary**

The middle-endotherm peak which appears in the DSC scans of annealed or heat-set materials can be a very useful tool to investigate the specific thermal history applied to the material. Modulated DSC separates the MEP into the Nonreversing Heat Flow signal, which improves the resolution of this entity. Using MDSC, several polymeric samples have been examined, and the thermal histories of these samples have been extrapolated back from the investigation of the middle-endotherm peak.
Thermal Hazard Information
required by US Federal regulation

Time to Thermal Runaway, Critical Temperature, Critical Dimension and Adiabatic Decomposition Temperature Rise are figures-of-merit used to assess the thermal hazard of chemicals or chemical process materials. ASTM Test Method E 1231 describes how these figures-of-merit may be calculated from DSC derived data including kinetics, specific heat capacity and thermal conductivity.

According to U.S. federal regulation, companies involved in chemical manufacturing or processing are now required to have thermal hazard potential information on all of their process materials. This means that many organizations, which were not formerly concerned about hazard potential (because their processes are considered to be safe), now need to initiate programs to obtain this information.

TA Instruments supplies analysis software for calculation of these important hazard potential parameters

The TA Instruments Thermal Solutions DSC Thermal Stability Kinetics software package includes these calculations as part of the program.

Copies of E 1231 may be ordered directly from ASTM by calling (610) 832-9585 or by writing to ASTM Customer Service, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959. Each copy will be priced at about 20 US dollars.

May '97 witnessed an achievement with the shipping of our 100th DMA 2980. This significant event, coming only seven months after the shipment of the first 2980, is a milestone worthy of celebration.

The high customer demand for this improved design is a credit to those members of the development team who made it possible. We would be remiss, however, not to acknowledge the excellent effort extended by the manufacturing team who turned this successful design into reality. Preliminary reports expect this to be the most successful product introduction in the history of TA Instruments.

An evening celebration of fine dining was held to commemorate the event. The festivities included presentation of a personalized framed photo of the instrument and team for all employees who participated in making the DMA a success. Speakers that evening included Len Thomas, the president of TA Instruments.

Most of all we wish to thank our customers. It is your insistence for quality that fires our imagination. The DMA 2980 represents the culmination of your needs and our commitment to satisfy them.

Select members of the development team shown with the 1000th DMA.