TA Instruments proudly introduced a new technology, Micro-Thermal Analysis, and the new µTA™ 2990 Micro-Thermal Analyzer at the Pittsburgh Conference in March. The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy is a major international event for the analytical instruments and laboratory equipment industry with approximately 30,000 attendees and over 1200 companies exhibiting their new products. The µTA 2990 Micro-Thermal Analyzer was selected from the many new introductions at the conference to receive the gold award as the Best New Product at PittCon ’98. Selection for this award by an independent panel of editors is evidence of the significance of this new technology.

Micro-Thermal Analysis combines the visualization power of atomic force microscopy (AFM) with the characterization capabilities of thermal analysis. In Micro-Thermal Analysis, the AFM head is fitted with an ultra-miniature temperature probe, which not only provides the heat source, but also measures response providing information similar to traditional thermal analysis but on a microscopic scale. Patented modulated temperature technology is used to enhance the signal in a technique similar to Modulated DSC®, and to provide depth profiling by varying the frequency over a wide range. This new technology has wide ranging applications including the characterization of phases, grains and interfaces of polymers, pharmaceuticals, and foods.

Micro-Thermal Analysis can be used to characterize materials and surfaces, (Continued on page 3)
Modulated TGA™: A Faster Approach to Obtaining Kinetic Parameters

One application of TGA is the estimation of product lifetime. TGA decomposition kinetics can provide useful aging stability information and lifetime predictions.

The TGA decomposition kinetics method (ASTM Standard E1640) uses the data from experiments run at several heating rates to calculate kinetic parameters, including activation energy and the specific rate constant. Limitations of this traditional kinetics method include the amount of time required for several experiments, and the fact that kinetic parameters are calculated as a single value, based on the assumption that a single decomposition mechanism controls the entire decomposition range of the material.

TA Instruments has recently introduced a new approach, Modulated TGA™ (MTGA™), which delivers superior kinetic analysis without the time and single decomposition mechanism limitations of the traditional technique. This patent-pending approach is the result of TA Instruments’ continuing commitment to technological innovation and leadership. MTGA™ shares its roots with the now widely accepted Modulated DSC® (MDSC®) technology. Like High Resolution TGA®, MTGA is available exclusively from TA Instruments as an optional capability that can be added to the TGA 2950 (shown at left).

In MTGA, a sinusoidal temperature modulation is superimposed on the traditional underlying 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 modulations. Evaluation of this rate of weight loss provides an experimental tool to study the kinetics of decomposition or volatile reactions. The MTGA approach can be combined with a linear or HiRes underlying heating rate to scan from one weight loss region to another. It can also be used under quasi-isothermal conditions to analyze a single weight loss.

Figure 1 shows the results of a Modulated TGA experiment performed on 60% EVA (Ethylene vinyl acetate) where a linear underlying heating rate was used. The plot shows the temperature modulation and the effect of that modulation on the rate of weight loss.

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 them to be studied as a function of other experimental parameters such as time, temperature, and conversion. Figure 2 shows the resulting Activation Energy vs Temperature plot from the MTGA experiment shown in Figure 1. Note that the activation energy changes throughout the decomposition process and from step 1 to step 2.

For additional information on Modulated TGA, contact your local technical representative, and request TA publications TA-237 & TA-245.
visualizing the spatial distribution of phases, components, and contaminants.

The instrument images a 100 x 100 µm region of the sample in terms of its topography, thermal conductivity, and thermal diffusivity. With a resolution of less than 1 µm, any point (2 x 2 µm) on the image can be selected for characterization of its calorimetric and mechanical properties.

Because each measurement affects a small amount of sample, heating and cooling rates are very high, providing the ability to make numerous measurements in a few minutes. Micro-Thermal Analysis is an important new addition to TA Instruments’ wide range of thermal analysis and rheology products. For additional information, contact your local technical representative.

Series 5000 Controllers

Just as the demands placed on today’s laboratories continue to increase, so too must the capabilities of the instrumentation. The challenges for today’s lab are to anticipate changing demands, and to respond in a timely, cost-effective manner.

Generating accurate analytical data is the primary function of laboratories. But, the real value of the analytical data is not realized unless it can be managed, stored, retrieved, transferred, shared, and presented in an easily understandable, publication-quality format.

The TA Instruments Thermal Analyst series 5000 controllers, powered by new Thermal Solutions™ for Windows NT® software, satisfies these diverse needs. It gives the user access to the complete line of TA Instruments innovative modules and specialty programs that have made TA Instruments the world’s leader in the field.

Continued Expansion

TA Instruments will celebrate its eighth birthday this year. During this time the business has more than doubled its sales, products and number of employees. For those of you that have visited our facility in New Castle, Delaware you know that we have run out of space.

The time has come to expand operations into a second facility. Located adjacent to our original building, the new location will initially house the Service Department. The newly available space at our original building will be utilized for a new applications lab (see our next issue), and an expanded R&D department.

Phone numbers and mailing address are not affected by the change.
Oxidative Induction Time
Reference Material Now Available!

In cooperation with ASTM Committee D9, a polyethylene film sample has been selected as a reference material for Oxidative Induction Time (OIT) testing. The OIT values of this material have been thoroughly tested by at least nine inter-laboratory test programs over a period of more than five years, making this one of the most well-characterized OIT materials. At present, this is thought to be the best reference material available for oxidative induction time testing.

OIT is a widely used parameter for the oxidative stability of polymers, edible oils, and lubricants. It is typically used as a quality control tool and to rank the effectiveness of various oxidation inhibitors. OIT is defined as the time to the onset of oxidation of a test specimen, exposed to an oxidizing gas at an elevated isothermal test temperature.

It is a kinetic parameter (that is, one dependent on both time and temperature) and is not a thermodynamic property. OIT measurements are affected by a number of factors (see publication TA 235), and it is not uncommon for results to vary widely between labs testing the same material. It is expected that inter-laboratory correlation will improve with the use of this well-characterized reference material.

This OIT reference material is available from TA Instruments as P/N 900319.901. Contact your local technical representative to place an order, or request publication TA 233 for additional information on the development of this new standard.

The TA Instruments Applications Laboratory
Characterization of Epoxy Prepregs by DSC

TA Instruments has helped customers use Thermal Analysis and Rheology to solve hundreds of materials characterization problems. The lab staff has recently begun to document some of these “Problems/ Solutions” as Thermal and Rheology Solutions (TA Publications with TS or RS prefixes). The goal is simply to share these brief practical applications to help you get the most from your investment in Thermal Analysis and Rheology.

A recent example (see TA Publication TS-34) involved samples of epoxy prepreg submitted by a printed circuit board manufacturer. Figure 1 shows two heat cycles on the epoxy prepreg. The DSC clearly detects a shift in the glass transition (Tg) temperature indicating that the sample, as received, was not fully cured. The under-cured sample could affect manufacturability (i.e., hole drilling) and end-use reliability.

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**

Dynamic Mechanical Analysis of polymers [Ref. No. TA236]
Modulated Thermogravimetric Analysis: A new approach for obtaining kinetic parameters [Ref. No. TA237]
Evaluation of Hazards Potential by DSC [Ref. No. TA238]
Certificate of year 2000 compliance - RMX Software [Ref. No. TN42]
Certificate of year 2000 compliance - Thermal Solutions Software [Ref. No. TN43]
Purge Gas Recommendations for use in Modulated DSC© [Ref. No. TN44]
Choosing Conditions in Modulated DSC© [Ref. No. TN45]
Thermal Solutions for Windows NT brochure [Ref. No. TA242]
µTA 2990 - Micro-Thermal Analyzer brochure [Ref. No. TA243]
Micro-Thermal Analysis - Thermal analysis for the 21st century [Ref. No. TA244]
Modulated TGA - A Faster approach to obtaining kinetic parameters [Ref. No. TA245]
Time-Temperature Superposition Theory [Ref. No. TA246]
Characterization of Epoxy Prepregs by DSC [Ref. No. TS34]

**Rheology**

Listing of Rheology Reference Books [Ref. No. RN12]
Certificate of year 2000 compliance - Rheology Solutions Software [Ref. No. RN15]
Rheology Navigator 2 & 2plus Software [Ref. No. RH017]
The use of the method of incomplete creep to assess the resistance to rutting of bituminous materials [Ref. No. RH061]
Normal force measurements on the Rheolyst series AR1000-N Rheometer [Ref. No. RH062]
Normal force measurements on the AR1000-N Rheometer Part II - Practical Tips [Ref. No. RH063]
Rheology Software Models (Oscillation) [Ref. No. RH064]
Energy Storage and Dissipation in Viscoelastic Materials [Ref. No. RH065]
Rheology & Stability for Oil-In-Water Systems

To be stable, oil-in-water emulsions need to display a yield stress, i.e., at very low shear rates, they behave more like an elastic solid than a viscous liquid. The forces applied to the continuous phase by the discontinuous phase due to gravity/buoyancy must be below the system yield stress, i.e., the forces must not be sufficient to disrupt the structure set up in the continuous phase by rheology modifiers or liquid crystalline gel networks. The relationship of emulsion yield stress to the size of the largest oil droplets is an important determinant of emulsion stability: the larger the droplets, the larger the yield stress required to maintain them in place and prevent the onset of phase separation. Some approximate guideline numbers are contained in Table 1.

Another way of looking at the same phenomenon is to use a cone-and-plate rheometer in oscillation mode to extract the magnitude of the elastic forces operating within the emulsion $G'$ (i.e., the extent to which the emulsion is behaving like a Newtonian liquid). These two parameters can be measured across a range of temperatures (Fig 1). Essentially an oil-in-water emulsion will be stable so long as the viscous forces are less than the elastic forces, i.e., the ratio $G''/G'$, also known as tan delta, is less than 1. The temperature at which tan delta climbs above 1 is the temperature at which phase separation will inevitably occur with time.

The linear viscoelastic properties of polymers are both time and temperature dependent. When considering a material for an application, many times we want to know how the viscoelastic properties will change over a long period of time (very low frequencies) such as months or even years. Other times, we want to know the viscoelastic properties under very high frequency (very short time) applications such as high speed impact strength. Often the response times of interest are inconveniently long or outside the measurable limits of the instrument.

However, there is an empirical relationship between the time and temperature dependent properties of viscoelastic materials known as the time-temperature superposition principle. Both time and temperature have a similar effect on the linear viscoelastic properties of polymers. At low temperatures, the relaxation processes of a polymer, as measured in both dynamic and transient (creep and stress relaxation) testing, take longer than at higher temperatures. The extent to which these relaxation processes are slowed or accelerated are sometimes in proportion to the magnitude of temperature decrease and increase respectively.

Time-temperature superposition (TTS) allows us to characterize the viscoelastic properties of a material at various temperatures over an experimentally convenient time or frequency range. The data taken at various temperatures can be superimposed to a reference temperature of interest to extend the time range of response. The curve created by superposition is called a “master curve” and represents the time response of the material at the reference temperature.

For more information request Publication TA-246

Choosing Conditions in Modulated DSC®

Applications Note now available:

Modulated DSC (MDSC®) provides a powerful enhancement to the standard DSC experiment. MDSC can simultaneously improve the sensitivity and resolution of the DSC experiment, in addition to providing heat capacity and heat flow in a single experiment. In order to obtain the maximum benefit from the MDSC experiment, however, optimal MDSC conditions must be chosen. A new Applications Note examines the protocol for choosing the correct MDSC conditions with respect to sample size, modulation period, underlying heating rate, and modulation amplitude. For a thorough, yet practically-oriented discussion of this topic, request TA Publication TN-45. Its a must read for all MDSC users.
Micro-Thermal Analysis (µTA™) is a new technique that combines the visualization power of atomic force microscopy (AFM) with the characterization capabilities of thermal analysis. Typically, there are two parts to a Micro-Thermal Analysis experiment. First, the AFM is used to image the surface of a sample, up to an area of 100 by 100µm. Secondly, localized thermal analysis experiments are performed on a small part of the imaged sample to characterize the sample’s thermal properties.

In µTA the standard AFM probe is replaced with a miniature resistive heater. This provides additional imaging modes over a conventional AFM as well as providing the heating source for, and measuring the response from, the localized thermal analysis experiments.

Fig 1 shows a schematic of the µTA 2990 thermal probe, which is capable of sub-micron resolution. The thermal probe is rastered (scanned) over the surface of the sample using an x-y piezo in order to generate an image of the surface. As the topography changes underneath the probe, a restoring voltage is applied to the z-piezo in order to maintain the position of a laser beam, bounced off a mirror on the probe, at the same point on a photo-detector. Each pass across the sample creates a height profile that is related to the surface topography of that pass. By creating multiple passes (rastering) over the surface, a quantitative 3D image is obtained. While imaging the sample’s topography, the probe tip is held at a constant average temperature, a little above that of the sample. Superimposed on that average is a temperature modulation of a few degrees at frequencies in the kHz range. The average of the DC signal is a function of thermal conductivity and the response to the AC modulation signal is a function of thermal diffusivity. Consequently, three images (views) of the sample are obtained simultaneously: topography, thermal conductivity, and thermal diffusivity.

These images can be used to visualize the surface of a material and provide quantitative information about the size of features, domains or contaminants that may be present. Additionally, the images are used to select specific areas to be characterized simply by positioning the probe and performing a localized thermal analysis experiment.

Multi-Layer Films
A typical application area for Micro-Thermal Analysis is the visualization and characterization of heterogeneous materials. The example given here is from the packaging industry. When considering which material to use for the packaging of foods, multiple requirements need to be met. For example:

- Appropriate mechanical integrity
- Provide a flavor and gas barrier
- Withstand cooking temperatures
- Withstand sub-ambient storage temperatures
- Surface that can be printed upon

Clearly, a single polymer film cannot meet all of these requirements and so multi-layer films are often used to fulfill the various demands of the consumer.

Figure 2 shows the topography and thermal conductivity images for a multi-layer packaging film typically used in the packaging of convenience foods. The construction of the film comprises a central gas and flavor barrier layer.
surrounded by HDPE and LDPE outer surfaces designed to accept printing ink. Thin (20 micron) slivers of material were cut and mounted on a metal stub so that a smooth 300 micron cross-section could be presented to the microscope for imaging and subsequent localized thermal analysis. The topography image clearly shows the multi-layer composition of the film, and the thermal conductivity image shows that there is a central layer of polymer flanked by two outer layers, with a possible intermediate, tie layer.

Having now visualized the surface of the sample, the thermal properties of each individual layer were measured “in-situ” using Micro-Thermomechanical Analysis (µTMA™). In a µTMA experiment the probe is moved (through software) to any specific point on the surface, and the probe deflection is measured while heating the thermal probe. As the sample expands or softens, the position of the thermal probe is measured on the photodetector resulting in a measurement that is analogous to traditional Themomechanical Analysis (TMA).

Figure 3 shows the softening temperatures obtained from each layer at a heating rate of 500°C/min. Such fast heating rates are possible because of the small sample size and low thermal mass of the thermal probe. The softening temperatures are indicative of each polymer present in the film. Curves 1 & 5 are typical of HDPE, curves 3 & 6 correspond to the EVOH layer, curve 2 (the tie layer) has a lower softening point than HDPE and is probably MDPE, curve 4 is obtained from the EVOH/tie layer interface, and the measured response is a combination of each material’s individual response. Clearly, this type of characterization of individual layers by thermal analysis would not be possible by any other means.

Thin Films

For larger or homogenous samples, the AFM head may simply be placed on top of the sample. Figure 4 shows the topography image of an overhead transparency made by a photocopier from a page in a book. The image area is 100µm by 100µm and is from the dot of the letter “i” that appears on the page. The top righthand side of the image is that of the plastic film, whereas the remainder of the image is largely toner from the photocopying process.

In addition to µTMA measurements, the µTA2990 Micro-Thermal Analyzer can also make Micro-Modulated Differential Thermal Analysis measurements (µMDTA™). Here, a modulated signal is applied to the underlying heating rate in a way that is analogous to Modulated DSC®. The information obtained from µMDTA experiments is complimentary to that from traditional thermal analysis experiments. MDSC® has proven to be very useful in separating a total heat flow signal into its reversing and non-reversing components, similarly µMDTA is useful in separating a total heat flow into spatial information.

Figures 5 and 6 show the µTMA and µMDTA data from the overhead transparency. Three local thermal analysis experiments were made, two of the plastic film and a third on an area of toner. The positions of the scans are labeled in figure 4.

Locations 1 & 3, for the substrate, show an expansion in the µTMA signal to around 225°C, followed by softening and melting. This is confirmed by the peak in the µMDTA signal with an onset of around 240°C. For location 2, the toner, there is a softening of the toner, commencing at 80°C, followed at higher temperatures by the melt of the polymer substrate. It is interesting to observe a feature in the µMDTA trace at around 150°C, which corresponds to the fuser temperature of the photocopier.

From this data, we can conclude that the base film is PET (rather than the cellulose acetate alternative) and the toner is likely to be a poly(styrene-co-butyl methacrylate) base.

The unique ability of Micro-Thermal Analysis to visualize and characterize specific areas, domains, components or contaminants of a sample make these types of analysis possible. Indeed, this exciting new technology has wide ranging applications in the polymer, pharmaceutical, and food industries.
Continuing our commitment to service and support in helping you solve material characterization problems, TA Instruments has announced the 12th Annual Rheology Symposium to be held June 1st thru 4th. Response in previous years has been overwhelming.

The symposium is designed for those familiar with the basic concepts of rheology who are interested in learning more about the theory and potential applications of this valuable technique. The symposium includes lectures by distinguished speakers from both industry and academia, instrument demos and consultations on attendees’ applications.

Register today using the response card included with this newsletter!

- Also available -
A series of free Viscosity & Rheology Testing Seminars. An eleven-city US tour, May 5-21, discussing the basics of how rheology will help quantify material properties and performance.

Info and registration for both events is available on the TA Instruments web site.
Technical Conferences

North American Thermal Analysis Society
26th Annual conference. September 13-15 at the Sheraton Cleveland City Centre, Cleveland, Ohio.
For information:
The Complete Conference, 1540 River Park Drive, Suite 111, Sacramento, CA 95815
(916) 922-7032

American Ceramic Society
100th Annual meeting and exposition will be May 3 - 6, 1998 in Cincinnati, Ohio.
For more information visit their web site – www.acers.org
or phone (614) 794-5854

Society of Rheology
70th Annual Meeting
Monterey, California
October 4 - 8, 1998
For more information visit their web site – www.umecheme.maine.edu/sor

Institute of Food Technologist
Atlanta, Georgia
June 20 - 24, 1998
For more information visit their web site – www.ift.org
or phone - 1-800-438-3663

International Coatings Expo
New Orleans, Louisiana
October 14 - 16, 1998
For more information visit their web site – www.coatingstech.org
or phone (610) 940-0777

American Association of Pharmaceutical Scientist
annual meeting and exposition will be November 14 - 18, 1997
New Orleans, Louisiana.
Call (703) 548-3000 ext. 435 for information or visit their web site at www.aaps.org

First International Symposium on Micro-Thermal Analysis
October 5 - 6, 1998
Loughborough University, UK

We are pleased to invite participants to this symposium. The team that invented Micro-Thermal Analysis will provide:

- An overview of how Micro-Thermal Analysis is used with conventional thermal methods and other forms of analytical microscopy
- Live practical demonstrations
- Latest theory and practice
- Updates on the state-of-the-art for use of Micro-Thermal Analysis for localized chemical analysis

Materials scientists seeking to explore possible applications of this new technology are welcome.

For further information please apply to:

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Telephone (44) 01509 223340
Fax. (44) 01509 223949

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and
www.lboro.ac.uk/departments/iptme/atmu/
email: j.a.baseley@lboro.ac.uk

Rheological Behavior of Polymeric Liquids with Laboratory Workshop
Course date: July 13 - 17, 1998
Massachusetts Institute of Technology

It is the purpose of this course to provide a practical and fundamental understanding of the viscoelasticity of polymeric fluids. The measurements of rheological material properties and their interrelationship with molecular structure will be emphasized. Practical methods for using rheological characterization to model processing steps will be illustrated. Modern methods for describing the rheology of these materials will also be covered. Particular attention will be given to use of constitutive equations in quality control and process control applications.

For more information call (617) 253-2101 or e-mail professional-institute@mit.edu

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For more information call (617) 253-2101 or e-mail professional-institute@mit.edu
First International
Pharmaceutical and Food Science Applications of Modulated DSC
September 28 - 29, 1998
University of London, UK

A two-day symposium at the School of Pharmacy. This course will offer:
• Basic introduction regarding the technique (theoretical and practical)
• Opportunities to have samples run and discussed
• Invited speakers who are at the forefront of MTDSC research in the pharmaceutical and food sciences
• An opportunity to discuss practical considerations informally with experienced operators
• An opportunity to present and discuss work, including ongoing studies which are not yet complete

For further information,
Dr. Duncan Craig
Telephone (44) 0171 753 5863
or e-mail duncraig@cua.ulsop.pharm.ac.uk

Viscosity and Rheology Testing Seminars
These seminars are provided free of charge by TA Instruments. Space is limited and registration is required, so respond today to reserve your space.

TUESDAY MAY 5, 1998
Boulder, CO Courtyard by Marriott
Princeton, NJ Hyatt Regency, Princeton

THURSDAY MAY 7, 1998
Los Angeles, CA Courtyard LA Airport

TUESDAY MAY 12, 1998
Chicago, IL Radisson, Schaumberg

WEDNESDAY MAY 13, 1998
Albany, NY The Desmond Hotel

THURSDAY MAY 14, 1998
Boston, MA Crowne Plaza, Natick
RTP, NC Holiday Inn, Plantation

TUESDAY MAY 19, 1998
Houston, TX Radisson, Hobby Airport
Detroit, MI Hilton, Novi

THURSDAY MAY 21, 1998
Atlanta, GA Cobb Galleria Centre
Kansas City, MO Embassy Suites

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