HOTLINE

Featured Technical Articles

TA Instruments Announces the Purchase of Rheometric Scientific

TA Instruments, the leader in thermal analysis and rheology systems, is pleased to announce our recent purchase of the Rheology Division of Rheometric Scientific, the world's most recognized rheology supplier.

More Information

Rheological Evaluation of Thermosetting Urethane Sealants

Dr. S. R. Aubuchon

A rheological characterization is presented of a thermosetting urethane sealant

manufactured for use in a medical device. Viscosity and viscoelastic data are presented to demonstrate the ability of the AR 2000 rheometer to monitor the curing profile of the urethane, and to aid in optimizing and trouble-shooting in the manufacturing process.

Full Article

Fast Scan DSC to Quantify Metastable Forms

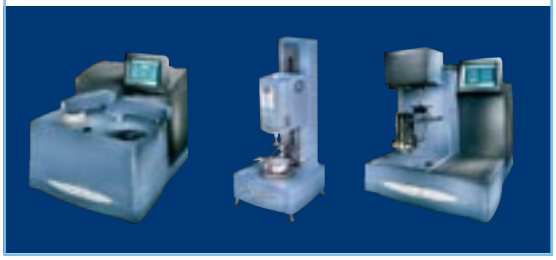
R. Bruce Cassel and Monika Wiese

Special interest has recently arisen in using DSC with faster heating and cooling rates to quantify the thermal characteristics of materials in metastable states. New technology, from TA Instruments, now permits this to be accomplished easily, and without resorting to extraordinary experimental conditions. Full Article

TA Instruments Expands *e-Training* Courses

TA Instruments has now added DSC Certified User Training to our portfolio of customer e-Training Courses. Learn more about these and all of our web-based courses, where our experts teach you how to get the most from your TA Instruments thermal analyzer or rheometer.

Full Article



Tech Talk

This section provides technical notes, application briefs, helpful hints, and specific information on the use of thermal analysis and rheology instrumentation. The goal is to help you get the maximum value from your TA Instruments' equipment.

Technical Documents

Available for easy download are a series of technical notes and applications briefs relating to various topics in thermal analysis and rheology.

Thermal Analysis

1. **Polymer Heats of Fusion (TN 48) –** this contains a listing of heats of fusion for a series of common polymers.
2. **General Procedure for Conducting Quasi-Isothermal MDSC® Experiments**
3. **DSC Detection of Polymorphism in Pharmaceutical Anhydrous Dexamethasone Acetate (TA 302)**
4. **DSC Step Annealing for Fingerprinting Molecular Structure in Poly (vinylidene fluoride) (TA 300)**
5. **Physical Aging and Fragility of Amorphous Polyethylene Terephthalate (TA 299)**
6. **Physical Aging and Fragility of Amorphous Sucrose (TA 296)**
7. **Improvements in DMA Measurements Using Low-Friction, 3-Point Bending Clamps (TA 301)**

Rheology

1. **Spectral Analysis and the Interconversion of Linear Viscoelastic Functions**
2. **Understanding Normal Force Control on AR Series Rheometers**

HINTS

Here is a way to find an old data file. Use the Search/Find function of Windows, (Search button on the toolbar in Explorer for Windows2000, or Explorer/tools/find/Files or Folders in NT 4.0) together with a keyword or phrase inserted into the "Containing Text" box. For example, if you want to see a list of all MDSC data files, search on "MDSC" over the range of file folders containing data. This will produce a list of all the MDSC data files that can then be arranged alphanumerically or chronologically by clicking over the appropriate columns. These files can then be selected and copied (Cntrl +c) to a remote archive such as a Zip removable disk. And you can generate a hard copy of this list by pressing Alt + Print Scrn which puts an image on the clipboard of the highlighted window, that can then be pasted (Cntrl +v) into Microsoft Word™/ Microsoft Paint™, or wherever for printing or saving to a file. For finding all data files generated at a particular heating rate, go into the line of the View/Parameter Block menu item in Universal Analysis, find the line that displays the heating rate, select and copy it. Paste it into the "Containing Text" line of the Search/Find function, then edit it to the desired rate and press Search Now or Find Now button.

Thanks to Bruce Cassel of TA Instruments for this Hint.

In Oxidation Induction Time (OIT) DSC experiments, the test specimen often "balls up" when it melts, changing the surface area exposed to the reactive air or oxygen. One tool for keeping the sample evenly spread is to crimp a small piece of aluminum screen over the sample as a porous "lid". Suitable screening for this purpose may be obtained from common hardware aluminum screen with a 6.3 mm (standard 1/4 inch) paper punch. Be sure to use only aluminum screen, however, as screens made from other metals may catalyze the OIT reaction.

Thanks to Ed Boyd (Noveon) for this Hint.

REWARDS FOR HINTS

This HINTS section, with its suggestions on how to do better or easier thermal analysis and rheology, has proven to be very popular. So we are looking for even more HINTS to pass along. Do you have one that you would like to offer? Send it to us and if we use it, we'll send to you a certificate worth $50 on your next purchase of supplies, services or equipment. Send your hints to **rblaine@tainst.com**.

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TA Instruments is committed to providing our customers with the latest technology. Highlighted below are new products and accessories now available:

Q400 & Q400EM Thermomechanical Analyzers

TA Instruments is pleased to introduce the TMA Q400 and Q400EM, two powerful and versatile analyzers that extend the Q Series™ measurement modules, and provide mechanical property measurements on a broad variety of materials from -150 to 1,000˚C. The Q400 is a rugged, easy-to-use analyzer that provides state-of-the-art performance in research or quality control applications involving dimension change measurements as a function of temperature, time, or force. The Q400EM is our premier, research-grade TMA. It delivers the same performance excellence in standard TMA operation, but also offers advanced operational modes, such as stress and strain ramps, creep, stress relaxation, dynamic TMA (DTMA), and modulated TMA™ (MTMA™). Complementing the Q400 / Q400EM performance is a broad range of easy-to-use sample measurement probes and fixtures, plus Thermal Advantage™, the industry's premier operating / data analysis software.

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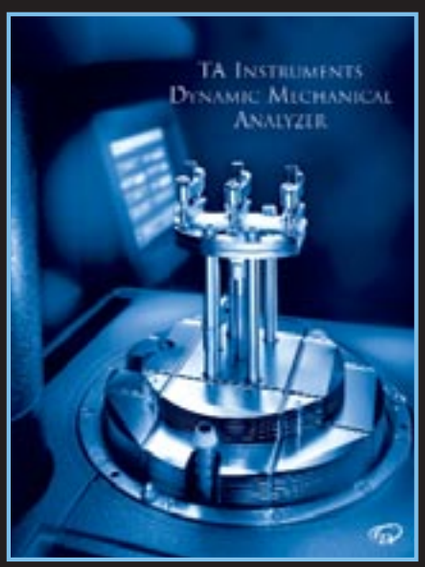
OVERVIEW

RHEOLOGY

DSC

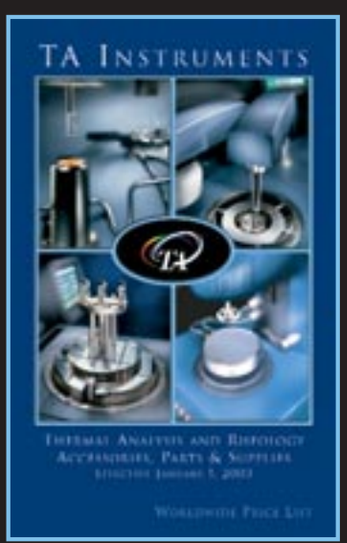
TGA



DMA

Training Brochure

Applicable in U.S. Only



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Price Guide

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Theory & Applications Training Courses

The TA Instruments Thermal Analysis and Rheology training courses (lecture-based) are designed to familiarize the user with applications, method development, and operating techniques of our thermal analysis and rheology instrumentation. Each course is specific to a particular technique and costs $400 per person, per day. New system purchases will include a waiver for one free class per instrument purchased. Typically, these courses should be attended within 3-6 months of purchase and assume the customer knows how to operate the instruments.

To register visit www.tainst.com/support/training.html (U.S. only)

2003 U.S. COURSE SCHEDULE

Thermal Analysis and Rheology Training Courses

DSC Advanced: Optimization of Experimental Conditions and Data Interpretation

Feb 27 May 1 Jun 12 Aug 21 Dec 11

DSC Basic: Theory, Instrumentation, Accessory, & Software Operation

Feb 25 Apr 29 Jun 10 Aug 19 Oct 14 Dec 9

MDSC®: Theory & Applications

Feb 26 Jun 11 Aug 20 Dec 10

TGA: Theory, Instrumentation & Applications

Feb 24 Apr 30 Jun 9 Aug 18 Oct 15 Dec 8

DMA: Theory, Instrumentation & Applications

Feb 28 Apr 28 Aug 22 Oct 16

Rheology: Theory, Instrumentation & Applications

May 2 Jun 13 Oct 17 Dec 13

TMA (Internet Training Course)

Part I – Feb 11 Part II– Feb 12

2003 EUROPEAN COURSE SCHEDULE

Date	Meeting	Type	Location/Country
18 February 2003	DSC Kurs	Training	Alzenau, Germany
19 February 2003	UA Software Kurs	Training	Alzenau, Germany
20 February 2003	TGA Kurs	Training	Alzenau, Germany
20 February 2003	Viscoelastic properties of materials	Workshop	Benelux
12-13 March 2003	DSC Course “Theory and Practice”	Training	Benelux
26 March 2003	Characterization of Pharmaceuticals	Workshop	Benelux
20 March 2003	Characterization of Food (French Language)	Workshop	Benelux
27 March 2003	Characterization of Food	Workshop	Benelux
11 March 2003	DSC Course	Training	Leatherhead (UK)
12 March 2003	MDSC Course	Training	Leatherhead (UK)
18 March 2003	TGA Course	Training	Leatherhead (UK)
25-26 March 2003	Rheology Course	Training	Leatherhead (UK)
4 March2003	Viscoelastic Properties of Materials	Training	Sweden

More Information: germany@tainst.com france@tainst.com info@taeurope.co.com spain@tainst.com belgium@tainst.com sweden@tainst.com

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New Staff at TA Instruments

TA Instruments continues to grow and add staff worldwide. Below are recent additions to TA Instruments.

Sales

Front row: Mike Golinar, Rudolf Mollema, and Craig Kalas
Back row: Matthias Qvaisser, Richard Nadaud, and Sean Kohl

Service

Front row: Brian Jeffries, Julius Olorunyomi, and Apollo Rasato (not present: Bruno Roccaldo)
Middle row: Gianfrancio Fabbian, Allen Glassman, and Michael Eiermann
Back row: Robert Hackathorn, Craig Werzen, John Wilson, and Mauricio Melo

Applications

Front row: John Suwardie, Ming Yao, and Chuck Rohn
Back row: Aly Franck, and Wei Xie

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Conferences and Exhibitions

TA Instruments participates in a wide variety of exhibits, conferences, and seminars around the world. At many of these functions, you have the opportunity to see our latest thermal analysis systems and rheometers. You also have a chance to interface with our worldwide network of sales, service, and applications support professionals who can answer all your questions. Click on the links below for additional information.

North America **Europe**

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North American Conferences and Exhibitions

Exhibits

Pittsburgh Conference

Conference: March 9 - 14, 2003 - Orange County Convention Center, Orlando, FL, USA. Please visit our booth # 2969, if you plan to attend. For more information on the conference call: 412-825-3220. To register on-line, visit: **www.pittcon.org**

ACS National Exposition

Conference: March 24 - 26, 2003 – Morial Convention Center, New Orleans, LA, USA.
Please visit our booth #111, if you plan to attend. For more information on the conference, or to register on-line, visit: **www.acs.org**

SPE ANTEC

Conference: May 4-8, 2003 – Nashville Convention Center, Nashville, TN, USA.
Please visit our booth #906 / 909, if you plan to attend. For more information on the conference, or to register on-line, visit: **www.antec.ws**

Pressure Sensitive Tape Council

Conference: May 7-9, 2003 – Washington Hilton & Towers, Washington, DC, USA.
Please visit our booth, if you plan to attend. For more information on the conference, or to register on-line, visit: **www.pstc.org**

National Plastics Exposition

Conference: June 23-27, 2003 – McCormick Place, Chicago, IL, USA.
Please visit our booth #10131, if you plan to attend. For more information on the conference, or to register on-line, visit: **www.npe.org**

Institute of Food Technologies

Conference: July 13-16, 2003 - McCormick Place, Chicago, IL, USA.
Please visit our booth #4668, if you plan to attend. For more information on the conference, or to register on-line, visit: **www.ift.org**

ACS National Conference

Conference: September 8-10, 2003 – Jacob Javits Convention Center, New York, NY, USA. Please visit our booth #255, if you plan to attend. For more information on the conference, or to register on-line, visit: **www.acs.org**

NATAS Conference on Thermal Analysis & Applications

Conference / Short Course: September 20-24, 2003 – Albuquerque Hilton Hotel, Albuquerque, NM, USA. Please visit our booth, if you plan to attend. For more information on the conference, or to register on-line, visit: **www.natasinfo.org**

Society of Rheology

Conference / Short Course: October 12-16, 2003 – Pittsburgh, PA, USA. Please visit our booth, if you plan to attend. For more information on the conference, or to register on-line, visit: **societyofrheology.org**

AAPS Annual Meeting

Conference: October 26-30, 2003 – Salt Palace Convention Center, Salt Lake City, UT, USA. Please visit our booth, if you plan to attend. For more information on the conference, or to register on-line, visit: **www.aaps.org**

International Coatings Exposition

Conference / Exhibition: November 12-14, 2003 – Pennsylvania Convention Center, Philadelphia, PA, USA. Please visit our booth, if you plan to attend. For more information on the conference, or to register on-line, visit: **www.coatingstech.org**

Conferences

NATAS / GGPF Spring Symposium

Thermal Analysis Short Course and Symposium: March 3-5, 2003 – Mountain View, CA, USA. Short courses include “Fundamentals of Thermal Analysis” and “Polymer and Pharmaceutical Applications”. Symposium includes “Recent Advances in Microanalytical Techniques”. Further details about the course content and the speakers can be obtained at **www.ggpf.org** or from Bruce Prime at **rbprime@attglobal.net**.

Getting The Most out of Thermal – Rheological Techniques

Conference: April 21 – 23, 2003 – Marriot Downtown Hotel, Chicago, IL, USA. For more information contact Innoplast Solutions (Tel: 912-280-0771; e-mail: **InnoPlast@aol.com**) or **download brochure**.

Integration of Analytical Sciences for Synergistic Impact on Industrial Problem Solving

Conference: May 19 – 21, 2003 – Headquarters Plaza Hotel, Morristown, NJ, USA. For more information contact Innoplast Solutions (Tel: 912-280-0771; e-mail: **InnoPlast@aol.com**) or **download brochure**.

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European Conferences and Exhibitions

Germany and Switzerland

Exhibits

Ulm – Freiberger Kalorimetrietage

Conference: March 19-21, 2003 – Freiburg, Germany

European Coatings Show

Conference: April 8-10, 2003 – Nurnberg, Germany

Achema

Conference: May 19-24, 2003 – Frankfurt, Germany

For further information on these conferences / exhibitions contact our German Manager, Wolfgang Kunze at **wolfgang_kunze@tainst.waters.com**

Great Britain

Conferences

TAC 2003

Conference: April 15 – 16, 2003 – University of Huddersfield. Materials and Instrumentation for the 21st Century. TA UK staff will present a paper on TGA / MS, and will sponsor an event.

Seminars

Welcome to TA Instruments: March 4, 2003 – A day for current users of Rheometrics instruments to visit TA Instruments, UK, at their Leatherhead facility.

Seminar of Viscoelasticity at TA Instruments (UK): April 8-9, 2003. Focus will be placed on the design, selection, and applications of fluids and solids rheometers.

TA Instruments User Meeting: June 29 – 30, 2003. Topics covered will include analysis of polymers, pharmaceuticals, and foods.

For further information on any of these topics, please contact TA Instruments (UK) at **info@taeurope.co.com**

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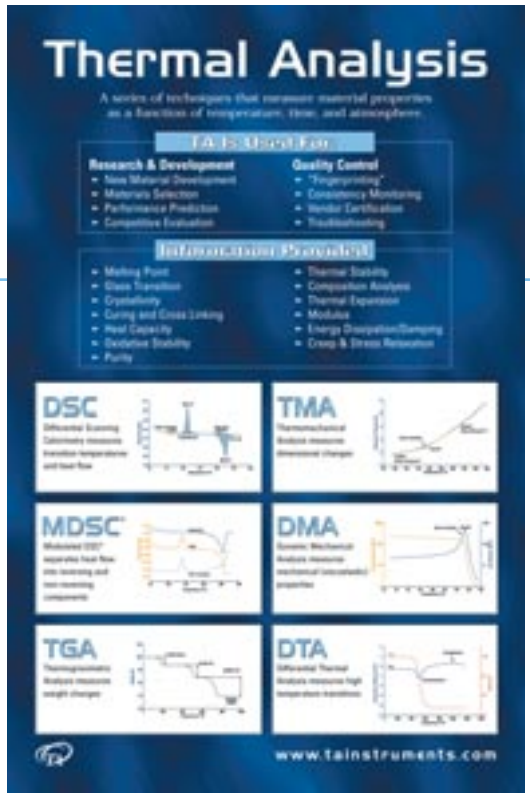
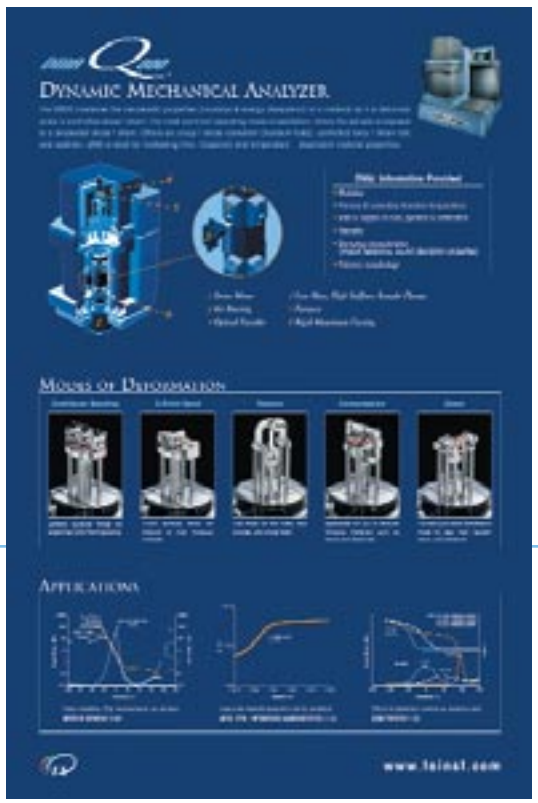
Rheology Poster



Thermal Analysis Poster



DMA Poster

Polymer Reference Card

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TA Instruments *e-Training* Courses

These courses offer a new way to learn or advance your knowledge of thermal analysis and rheology in the convenience of your office or home. Just use your computer to log onto a website, join a teleconference, and participate in a training presentation given by an experienced applications specialist. TA Instruments offers a portfolio of live courses where presentations are viewed over the Internet, and the audio is heard via a teleconference (U.S. phone number). This affords interaction with the instructor. We also offer pre-recorded courses on a 24-hour basis, for those who cannot attend the live versions. These allow viewing the presentation and listening to the audio via a computer (sound card and speakers required). As an introductory offer, you can attend any of our courses at a 50% discount if you sign up prior to March 28. Details of the offer are provided below. TA Instruments e-Training opportunities include:

QuickStart e-Training Courses

These are designed to teach a new user how to set-up and run samples on their TA Instruments thermal analyzer or rheometer. The 60-90 minute courses are offered regularly, and cost $250 for the live courses, and $125 for the pre-recorded versions. New system purchases will include a waiver for one free class per instrument purchased. We recommend that these courses be taken soon after installation.

Courses are available for:

- **Q Series™ DSC, TGA, SDT, and DMA thermal analyzers**
- **AR Rheometers**
- **Universal Analysis (UA)**
- **Rheology Data Analysis (RA)**

Attendees will receive the following:

- **A basic understanding of the instrument**
- **Instructions on set-up, running, and analyzing data for a typical experiment**
- **Instructions on calibration, routine maintenance, and tips on sample preparation**
- **Instructions on using the extensive, built-in help system**

Register now for Live Courses

Register now for Pre-Recorded Courses

Advanced e-Training Courses

We also offer several courses to advance your training to the next level. These 60-90 minutes courses cost $300 live, and $150 pre-recorded. They assume a basic understanding by the user and have pre-requisites as listed below. Current courses are:

Modulated DSC®

Attendees gain a basic knowledge of the MDSC technique including theory, calibration, experimental conditions, and data interpretation. Pre-requisite of DSC QuickStart (or equivalent knowledge).

Advanced UA Part I

This course provides additional instruction on the use of Universal Analysis with sections on displaying thermal analysis data, analyzing data, and reporting of results. Pre-requisite of UA QuickStart (or equivalent knowledge).

Advanced RA Part I

This course provides additional instruction on displaying rheology data, analyzing data, reporting results, mathematical modeling of data, and Time Temperature Superpositioning (TTS). Pre-requisite of RA QuickStart (or equivalent knowledge).

Register now for Live Courses

Register now for Pre-Recorded Courses

DSC Certified User Training

In a continuing effort to help our customers achieve a higher level of expertise, TA Instruments is proud to announce our latest training courses designed to help you get the most from your DSC instrument. Our DSC Certified User Series comprises four sections taught by our knowledgeable applications staff. These 75-90 minutes sections will each cost $300, and consist of:

- **DSC - Theory**
- **DSC - Calibration & Maintenance**
- **DSC – Method Development**
- **DSC – Data Interpretation**

An exam will be given at the end of each section. Upon passing all four sections, a Certificate will be issued stating that you have completed TA Instruments Certified DSC program. This certificate will be good for 2 years from the date of issuance.

Register now for Live Courses

We are pleased to offer these programs and the training opportunities that they afford our users. We will add further courses throughout the year, so please check our website periodically for updates. **http://www.tainst.com/support/training.html**. We look forward to working with you to ensure that you get the most out of your thermal analysis and rheology instrumentation. If you have any questions or need further information, contact us at **training@tainst.com**.

SPECIAL OFFER

As a special offer to Hotline readers, register for any of the e-Training courses before March 28th and receive a 50% discount. To take advantage of this offer, follow the links below and use the appropriate Coupon Codes (case sensitive):

Register for Course	Coupon Code
Live QuickStart Course	qslive
Recorded QuickStart Course	qsrec
Live Advanced Course	adlive
Recorded Advanced Course	adrec
Live Certified DSC Course	certdsc

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Rheological Evaluation of Thermosetting Urethane Sealants

Steven R. Aubuchon
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ABSTRACT

The rheological characterization is presented of a thermosetting urethane sealant used in a medical device. The manufacturer is interested in the time-to-cure and the viscosity profile of the urethane as a function of time and/or temperature. Both viscosity and viscoelastic data are presented demonstrating the utility of the AR2000 rheometer (with ETC oven and disposable plates) to monitor the curing profile of the urethane, aiding in the optimization and trouble-shooting of the manufacturing process.

INTRODUCTION

Urethane-based thermoset polymers are used as adhesives and sealants because of their desirable chemical and mechanical properties. Often, these materials can be delivered as uncured resins of low viscosity, and allowed to cure *in situ*, resulting in an excellent molded sealant application. However, the uncured monomer is often highly reactive at ambient conditions, and as such manufacturing conditions must be highly regulated. For example, feedstock urethane resin must be kept frozen, to suppress pre-cure, and rapidly delivered to the mold to insure optimal post-cure performance.

One manufacturer of medical devices uses a polyurethane sealant in a heat-exchange device often used during open-heart surgery. Because of the medical application, there is zero-tolerance for failure of the sealant as this could result in biological contamination. To improve production quality and product performance, the AR2000 Advanced Rheometer is used as a tool to monitor the quality of incoming feedstock, and to optimize production conditions.

EXPERIMENTAL

All rheological analyses were performed with the AR2000 Advanced Rheometer, equipped with the Environmental Test Chamber (ETC). Because of the thermosetting nature of the material, 25 mm disposable plates were used as the test geometry. The urethane samples were supplied by the manufacturer, and were analyzed under a flowing atmosphere of dry nitrogen.

RESULTS AND DISCUSSION

The urethane resin is supplied frozen in a large tube. During the manufacturing process, the tube is heated for *ca.* 30 min at 50 °C in a warming oven to melt the resin, and then the tube is placed in a large pneumatic syringe for injection into the product. The product is then centrifuged to evenly disperse the urethane, and finally baked under a proprietary set of conditions, to finalize cure. The viscosity of the urethane is monitored

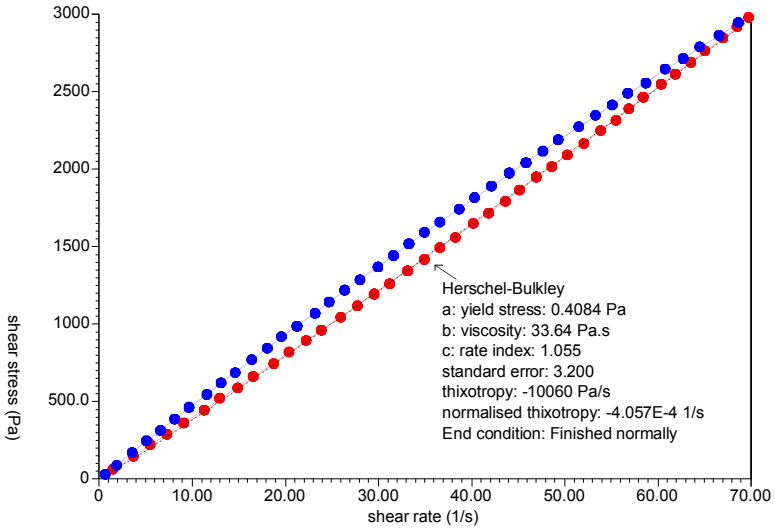

Figure 1 - Flow Behavior of Urethane Resin

at room temperature after removal from the warming oven (modeling the transfer process), then under a slow temperature ramp and finally at 50 °C (modeling the injection and centrifuge processes). Subsequent to these experiments, fresh samples are analyzed under oscillation to monitor the urethane cure during a controlled ramp from ambient to

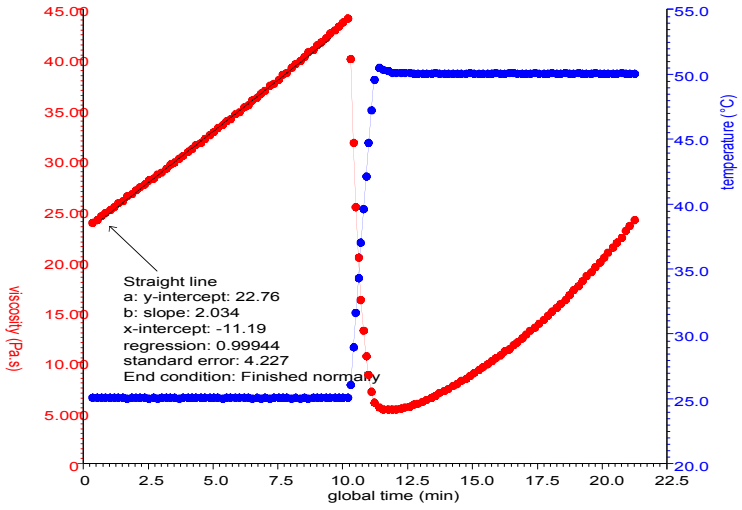

Figure 2 - Viscosity Profile of Urethane Resin

100 °C, and a isothermal hold of 15 minutes.

A sample of urethane is initially analyzed in a controlled stress flow (up/down) experiment at 25 °C to determine the degree of thixotropy or shear thinning in the uncured resin. Figure 1 contains the results. It is clear from the data that the uncured

urethane follows the Herschel-Bulkley flow model with minimal yield stress or shear-thinning. It is assumed that the measured viscosity is negligibly dependent on shear stress. (The increase in viscosity on the "down" curve is most likely due to residual curing of the resin).

To model the viscosity profile of the resin as it is delivered into the mold, a series of samples are run under the following profile: The frozen sample is heated in a 50 °C warming oven for ca. 30 min. An aliquot is removed and quickly placed on the measuring geometry at 25 °C. The sample is placed under a steady shear stress of 1 kPa for 10 min at 25 °C, and then heated at 25 °C/min to 50 °C, where it was held isothermally for an additional 15 min. This heating profile is intended to model the temperature experienced by the sample during the injection and centrifuge stages of production. Figure 2 contains representative data collected during this test.

It is noted from the data in Figure 2 that the viscosity of the urethane increases during the initial ambient isothermal period at a rate of ca. 2.6 Pa.s/min. The viscosity drops as expected on heating to 50°C, then climbs again as the sample undergoes further curing. This test is performed on sample that is held for varying times in the warming oven, to compare the viscosity dependence on preparation time. The results are shown in Figure 3.

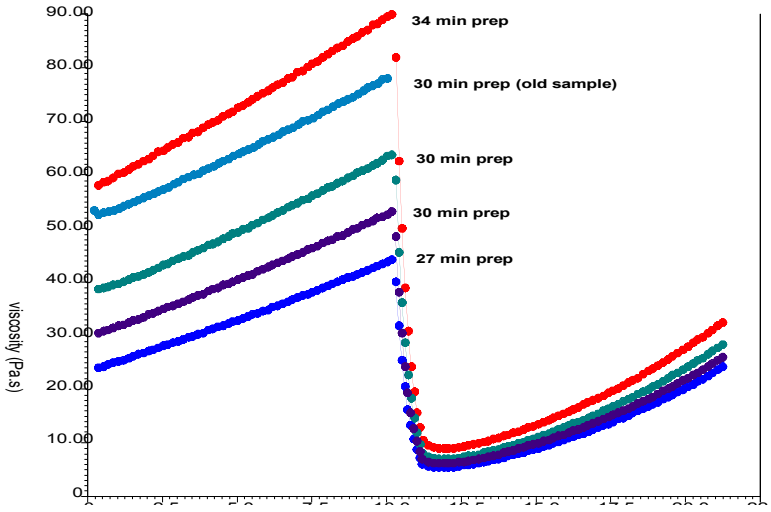

Figure 3. Comparison of Viscosity Profiles with Varying Preparation Times (noted on plot)

It is evident from the results of Figure 3 that the preparation time has a profound effect on the initial viscosity of the urethane. In addition, analysis of the slope of the viscosity increase during the initial isotherm suggests that the rate of the curing reaction is also a function of the preparation time (see Figure 4).

Understanding the rheology of the resin prior to injection and during the centrifuge process is paramount to optimizing the flow performance during this process. It is apparent that the handling time prior to injection greatly affects the viscosity of the urethane, and will subsequently impact resin performance in the manufacturing cycle.

In addition to flow performance, the curing times during the subsequent baking cycle is also of interest. The extent of cure can readily be monitored with an oscillation test. The relative magnitudes of storage modulus (G') and loss modulus (G") are good indicators of the rheological state of the material. When G" is greater in magnitude, the material is behaving more as a liquid. Conversely, if G' predominates, the material has more solid characteristics. During a thermoset process, G" will initially predominate in the uncured resin. As the curing process proceeds, G' will increase at a faster rate than

G" as structure is formed. At some point, a "crossover" will occur, after which G' is predominant. This crossover point is often referred to as the "gel point", and empirically represents the "halfway" point between liquid and solid. The gel point time (or temperature) is a useful parameter for monitoring the extent or rate of cure.

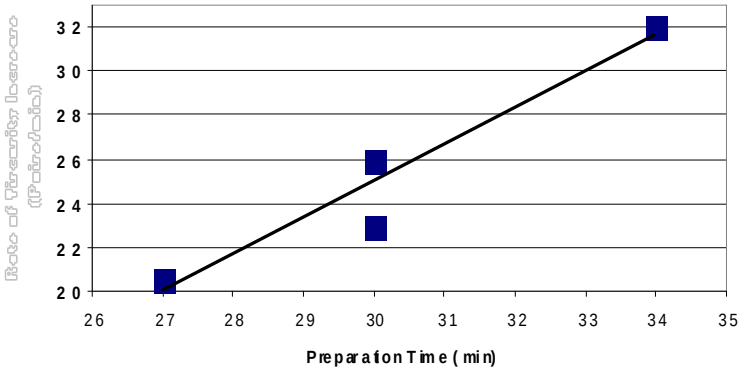

Figure 4 - Plot of Rate of Increase in Viscosity versus Preparation Time

Figure 5 shows the rheological data from the curing profile. In this experiment, the urethane sample was warmed and transferred as before. The sample was analyzed under oscillation conditions of 0.1 % strain at 1 Hz while heating at 5 °C/min to 100 °C. At this temperature, the strain was increased to 1.0 %. G', G" and complex viscosity (μ*) are monitored.

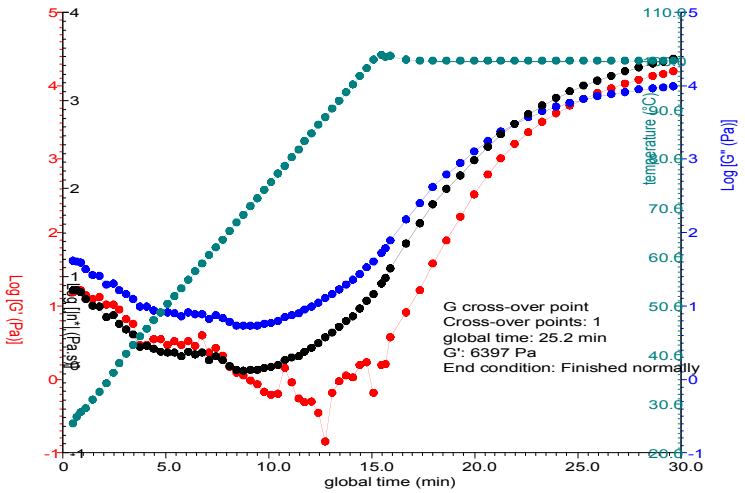

Figure 5 - Curing Profile for Urethane Resin

The data in Figure 5 show a marked change in G', G" and μ* as a function of temperature and time. G' increases nearly six orders-of-magnitude during this process. The AR2000 rheometer is fully capable of accommodating this million-fold change in modulus, as it utilizes both low-end sensitivity and high-end torque. The complex viscosity undergoes a four order of magnitude change as well during the curing process. The crossover point (gel time) is encountered at 25.3 min. Interestingly, on analyzing samples of varying preparation time, the gel time is consistently 25.3 min. This indicates that variance in preparation time does not affect the ultimate curing profile of the urethane.

CONCLUSION

A series of rheological tests on a urethane sealant shows that manufacturing variances are associated with the initial viscosity of the uncured resin, and this was a function of preparation time. The curing time was not affected by the preparation time of the urethane resin.

KEYWORDS

cure, flow properties, rheology, thermoset polymers, urethane polymers

Fast Scan DSC to Quantify Metastable Forms

R. Bruce Cassel
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And
Monika Wiese
TA Instruments, Max-Planck Str.11, 63755 Alzenau, Germany

Differential Scanning Calorimetry (DSC) has long been used for material characterization, especially to quantify the melting behavior of polymer formulations and pharmaceutical compounds. Recently there has been special interest in using the DSC with faster heating and cooling rates to quantify the thermal characteristics of materials in metastable states. New technology allows this technique to be carried out easily and without resorting to extraordinary experimental conditions (1).

Use in polymer analysis.

When materials are processed, they often end up in a thermodynamic state other than the most stable one. In the case of polymers, the last step in processing may be a rapid cool-down, which leaves the material with an imperfect semi-crystalline structure. When such a sample is heated it will undergo crystallization processes to achieve a more stable, low energy form. As a result, the DSC trace reflects the net heat flow from both melting and crystallization. One well-established technique to separate these two effects is MDSC®, which produces separate curves for reversible melting and non-reversing crystallization. However, this process of slow heating—in either DSC or MDSC—destroys the metastable, imperfect states which in fact contribute to the properties of the material as processed, and contributes other structures that were not present in the initial material. Hence, it can be argued that slow heating destroys potentially useful structural information. If, however, the DSC scan is carried out at a sufficiently fast heating rate, then the kinetically controlled crystallization processes can be minimized. Crystallization simply does not have time to take place.

An example of a material familiar to many thermal analysts is amorphous polyethylene terephthalate (a-PET), since its melting curve is often used in training courses. Figure 1 shows a sample of a-PET from a two-liter beverage container run at heating rates of 10, 50, 100 and 150°C/min after shock cooling the sample from the melt. The 10°C/min trace shows the well-known exothermic cold crystallization peak above the glass transition followed by the melting of the just-crystallized material. The 50 and 100°C/min traces show partial crystallization followed by reduced melting. The data taken at 150°C/min shows little or no crystallization and only a small amount of melting. If there is no evidence of crystallization, any melting endotherm is due to residual crystallinity, a useful parameter to determine. While initial crystallinity can be measured by other means, this fast rate method has the potential to be more accurate. Moreover, the fast DSC analysis is capable of giving specific heat data that is more representative of the material in its initial state.

Unlike PET, most semicrystalline polymers do not show the extreme differences in specific heat capacity when heated at fast and slow rates. However, the small

differences that are observed may provide insight into quality problems that relate to differences in processing. For example, polyolefin formulations may be characterized by the peak melting temperature, the melting onset and endpoint, and the fraction melted at a given temperature. But these parameters may be shifted by the thermal history, the cool-down history of the formulation. The use of fast rate DSC analysis provides data that better represents the initial crystalline morphology of the material. Figure 2 shows an example of a polypropylene sample cooled rapidly from the melt then heated by DSC at 10°C/min, cooled rapidly again, then heated at 100°C/min. Notice that while the melting peak is expected to be higher at 100°C/min because of thermal lag, it is seen to be several degrees lower because the faster rate inhibits crystallization during heating, which at 10°C/min results in more stable, higher melting crystals. The 100°C/min scan is thus more representative of the crystallite structures in this shock-cooled sample.

Use in pharmaceutical polymorph analysis

In pharmaceutical laboratories the motivation for using fast heating rates is different. In documenting the physical properties of drug candidates and excipients it is important to characterize all possible polymorphic forms (2). When an unstable polymorph is formed (e.g., by crystallization from a particular solvent system) it frequently reverts to a more stable form when heated. Use of a fast DSC heating rate sometimes allows the melting endotherm to be completed before the unstable material converts. This allows the thermodynamic parameters, C_p, T_m and ΔH_m to be determined for the metastable polymorph. This data is important to developing a phase diagram for the material and for predicting the relative stability of the polymorphs as a function of temperature. An example of this methodology can be seen in Figure 3 in the analysis of dexamethasone acetate, an anti-inflammatory agent. At 10°C/min, the low temperature melting polymorph exothermically converts to another form as it begins to melt, while at 150°C/min, the low temperature polymorph melts completely with little or no conversion to the more stable form.

Problems with fast DSC rates.

There are several instrumental and procedural difficulties associated with fast rate DSC techniques. The underlying problem is that fast scanning rates produce large temperature gradients due to thermal lag. For example, with the DSC cell and sample being held isothermally at the starting temperature, the controller commands a heating rate of 100°C/min. Initially the set point for furnace control begins heating at 100°C/min. The furnace lags behind the set point temperature; the surface that supports the sample pan lags behind the furnace, the sample pan lags behind the DSC cell, and there are even temperature gradients across the sample specimen itself.

Left uncorrected, these thermal lags result in grossly broadened peaks and uncertainty in temperature data. An additional concern is that the sample should achieve a constant heating rate before the data being acquired will be accurate. The magnitude of these errors is roughly proportional to heating rate, sample size, pan mass, and to thermal resistances in the system. To minimize errors to the point that the data is accurate enough to be useful requires correction for instrumentally caused error; and it requires careful sample preparation to minimize errors associated with specimen encapsulation. Some of the steps reported to minimize these errors are the use of foil instead of a sample pan for encapsulation, the use of grease to couple the foil to the DSC; the use of a neon purge gas mixture to enable the use of liquid nitrogen coolant over the temperature range required; and the reduction of sample mass to sub-milligram levels (3).

New DSC Technology

For those using recent DSC technology, none of these steps is necessary to achieve heating rates up to 150°C/min (1). TA Instruments' advanced Tzero™ Technology provides a unique capability to perform fast rate DSC analysis with a minimum of operator difficulty. The Q1000 DSC incorporates a sensor system that measures and compensates for thermal lags using a uniquely positioned, independent, null point ("Tzero") thermocouple, in addition to ΔT thermocouples (Figure 4). After an initial calibration of thermal characteristics of the sensor, the recorded temperature signal corresponds to the temperature of the sample pan—not to a sensor embedded in the DSC which is normally all that is available. Moreover, the heat flow signal is compensated to minimize the smearing (peak broadening) effects caused by cell and capsule capacitance. The Q1000's heat flow signal is the output of a four-term heat flow equation which takes into account the specific thermal characteristics of the DSC cell and capsule being used (4).

The difference that this makes for fast-scan DSC can be readily seen by running the indium calibration material at high scan rates. Figure 5 shows indium scans at 50, 75, 100 and 150°C/min using both sets of signals, those from only the ΔT output and those with the Tzero output (labeled T4P since they are the output of the four-term heat flow equation.) The result of Tzero technology is faster equilibration, sharper melting peaks and better resolution. Also notice that the melting point of indium, the peak onset temperature used for calibration, is essentially independent of scanning rate—heating or cooling--even at these rapid scan rates.

SUMMARY

There has been interest lately in performing DSC analyses at faster heating rates. The ability to use fast scanning rates provides the DSC technique with an additional tool for structure elucidation and problem solving. It also increases sensitivity for the analysis of small samples, and improves laboratory productivity. Fast scan rates have conventionally been associated with a major increase in errors due to sample and baseline effects. Advanced Tzero technology provides automatic compensation for thermal lag effects that are the major source of error in fast rate DSC. The use of the Q1000 with Tzero Technology, together with careful encapsulation in a standard pan, has been shown to allow accurate data to be obtained at heating rates of up to 150ºC/min, without the need to use operator-intensive, foil-and-grease techniques. Experimental details and further explanation of the technique are available in the references and from TA Instruments.

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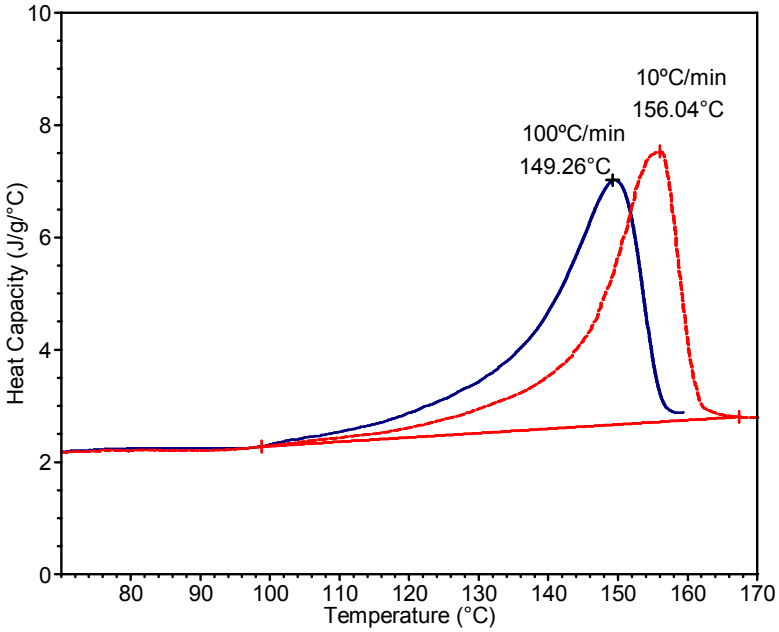

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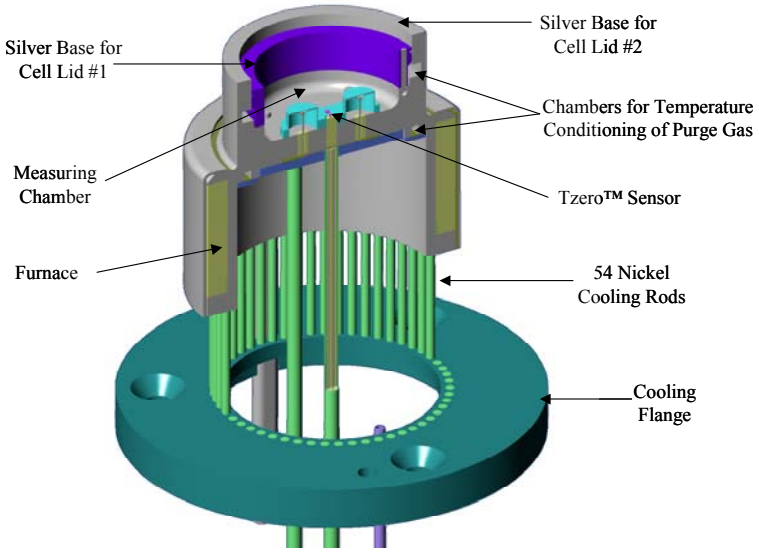

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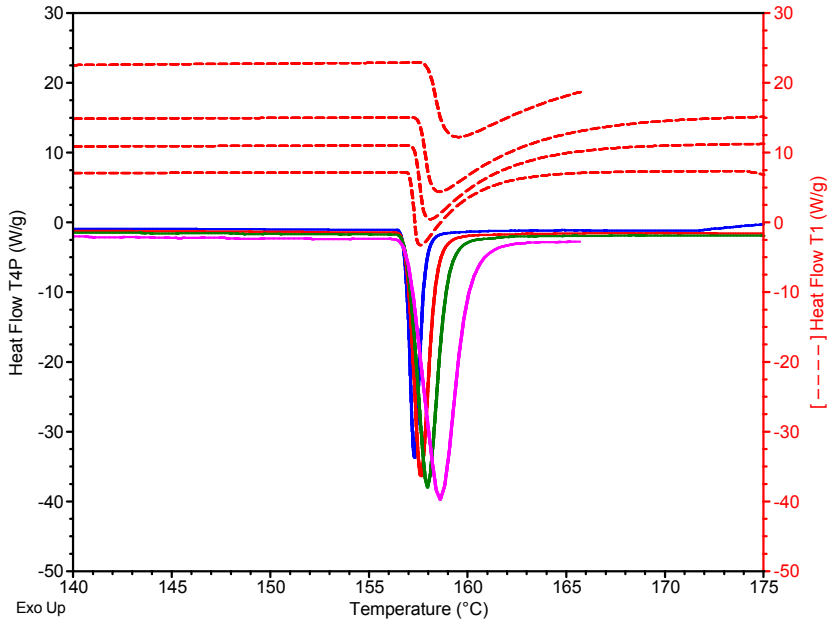

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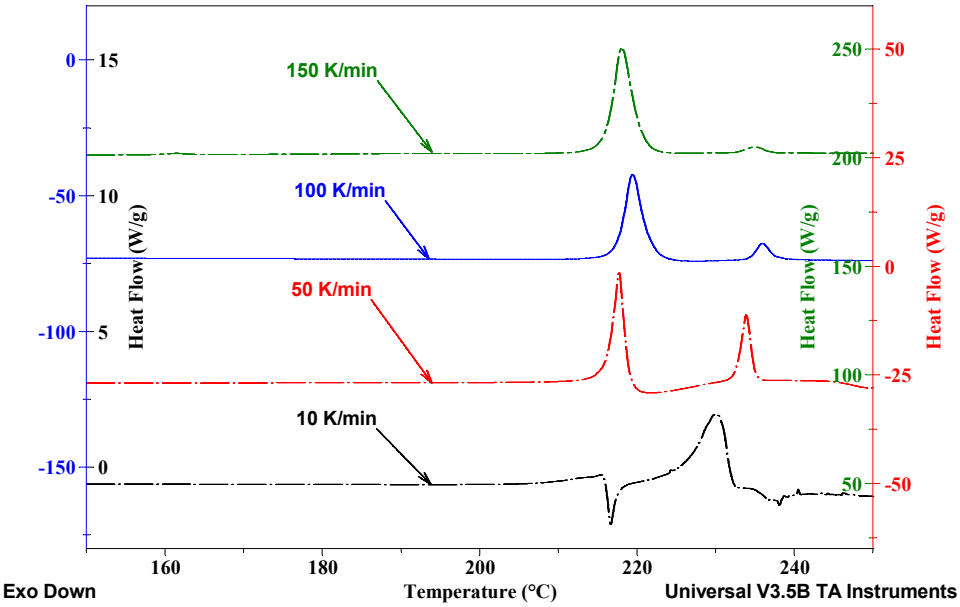

Figure 3

Figures

Figure 1. DSC of amorphous polyethylene terephthalate at four heating rates. Slower rates allow more time for crystallization. (Data is in units of specific heat, but curves have been shifted for clarity.)
Figure 2. Specific heat capacity data of rapidly cooled sub-milligram sample of polypropylene scanned at 10 and 100°C/min
Figure 3. DSC Heat Flow Anhydrous Dexamethasone Acetate heated at 10, 50, 100 and 150°C/min. (Y-axis scaling is adjusted to normalize for heating rate.)
Figure 4. Tzero™ Schematic Cross section
Figure 5. Melting indium at 50, 75, 100 and 150ºC/min showing the output of the Advanced Tzero signals and the conventional DSC ΔT signals (broken lines) at an expanded scale

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