Synergy of the combined application of thermal analysis and rheology in monitoring and characterizing changing processes in materials
Dr. Aly Franck and Wolfgang Kunze

Thermal Analysis and Rheology are complementary analytical techniques for the characterization of chemical processes. This paper shows their synergy for studying the structural changes and conversion found in the crosslinking reaction of thermosetting resins.

Full Article

Limitations of DSC for the measurement of Polymer Crystallinity
Len Thomas

The ability to correctly determine crystallinity in polymers is one of the many advantages Modulated DSC® offers over standard DSC. This article illustrates the problems thermal analysts may face in attempting to measure crystallinity by standard DSC and how MDSC may be used to overcome them.

Full Article

DSC Methods to Quantify Physical Aging and Mobility in Amorphous Systems: Part II-Assessing Molecular Mobility
Dr. Bruce Cassel

The specific heat capacity of amorphous sucrose was determined after annealing at a particular temperature within the glass transition (Tg) region. Enthalpic recovery after physical aging was obtained through the Tg region after several aging times. Values of the mean molecular relaxation time and a parameter for their distribution at the annealing temperature were also determined.

Full Article

How Tzero™ Technology Improves DSC Performance Part VI: Simplifying Calibration for Cooling Experiments
Dr. Bruce Cassel

Thermal lag between sample and reference temperature control sensors requires calibration of most DSCs at the heating rate to be used, or at multiple rates, to correct for this effect. It is also a concern in cooling experiments. This article shows how Tzero™ Technology used with a liquid crystal sample can provide calibration independent of heating or cooling rates.

Full Article
North American Conferences and Exhibitions

Upcoming Conferences
A selected listing of conferences that should interest thermal analysis and rheology users is shown below. TA Instruments will be participating as lecturers or exhibitors showing our latest thermal analysis and rheology products. For more information on European conferences contact our specific country contacts.

Exhibits/Conferences

User Meeting and Technical Symposium on Thermal Analysis and Rheology
Customer interest is rapidly rising over the special User Meeting and Technical Symposium on Thermal Analysis and Rheology that TA Instruments will sponsor at the La Mansion Hotel in San Antonio, Texas, USA from February 2 - 4, 2004. The 3-day symposium will feature lectures from a group of world-renowned experts. The program involves parallel thermal and rheology sessions, with lectures on polymers, foods, pharmaceuticals, and hazardous materials. In addition, we encourage the attendees to plan to present their own work at a poster session, take a TA User Certification Course, learn more about standard materials for thermal analysis, and hear the latest views on government compliance issues.

Current listings of lecture titles, abstracts, and biographies of our panel of distinguished speakers are available at www.tainst.com/2004usermeeting/user_meeting2.html. This promises to be an event-to-remember, and one that you will want to attend. For further details on the symposium and registration information please visit our website at www.tainst.com/2004usermeeting/ or contact Jane Bolmeye (phone: 302-427-4189 email: jbolmeye@tainstuments.com). We look forward to seeing all of you in San Antonio.

The Principles & Practice of Freeze-Drying
Workshop: January 6 - 8, 2004 – University of Connecticut, Storrs, CT, USA.
For more information on the workshop, or to register online, visit: http://www.ftssystems.com/seminars.htm.

Pittsburgh Conference
Conference: March 7 - 12, 2004 - McCormick Place, Chicago, IL, USA.
TA Instruments will display our latest line of Q Series™ Thermal Analyzers and Rheometrics Series Rheometers. If you will be visiting Pittcon, please plan to visit us at booth #1460. For further technical or general information on Pittcon, call 412-825-3220 or visit: www.pittcon.org

ACS National Exposition
Conference: March 28 - April 1, 2004 – Anaheim, CA, USA.
Please visit our booth if you plan to attend. For more information on the conference, or to register online, visit: www.acs.org

SPE ANTEC
Conference: May 16 - 20, 2004 – Navy Pier and Sheraton Chicago Hotel & Towers, Chicago, IL, USA.
Please visit our booth if you plan to attend. For more information on the conference, or to register online, visit: www.antec.ws
Technical Documents & Hints

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.

1. Modulated TMA™ - Measuring Expansion and Contraction at the Same Time (TA 311a)
2. Thermal Conductivity Measurements of Conductive Epoxy Additives by MDSC® (TA 312)
3. Physical Aging and Fragility of Amorphous Polyethylene Terephthalate (TA 299)
4. Isothermal Crystallization Using the Q Series™ DSC and Liquid Nitrogen Cooling System (TA 280)

HINTS

Everyone recognizes a glass transition in DSC when it takes the classic sigmoidal shape or when there is a dramatic step in the heat flow. But “real world” samples are seldom so well defined. Sometimes the glass transition is weak and broad, making its detection difficult. And sometimes one wonders whether there is a glass transition there at all. Here are a few steps to aid in the detection of the glass transition.

1. Make sure the empty pan baseline is straight. If not, run a baseline and subtract it from the thermal curve of the unknown sample. Maybe what you think is a glass transition comes from the baseline.
2. Prepare as large a sample as practical.
3. After heating the sample through the apparent glass transition region, stop heating and cool the sample slowly (2 °C/min) to well below the glass transition region. Next heat the sample at a high heating rate (e.g., 20 °C/min) from a temperature well below the anticipated onset to the glass transition. This should produce a long pre-transition baseline that will make the glass transition more obvious.
4. Improving on this set of conditions will be difficult without the use of MDSC, and an underlying heating rate of 10 °C/min.

   Thanks to Bruce Cassel (TA Instruments) for this Hint.

Clamping thin fibers for DMA or TMA work is always a challenge. Here is a hint to help you out. Place on the bench small strips of 3M Post-it Notes® (about 1 cm in length by 0.5 cm width) with the adhesive face up. Press the fiber onto the adhesive part of the paper and fold it over. Do this to both ends of the fiber. Using tweezers, pick up the prepared specimen by one of the small pieces of Post-it Note. Lower the specimen down into the upper clamp and tighten gently while the paper is above the clamp face (so the fixture is only clamping the fiber). “Float” the lower probe and raise it so the other piece of paper drops below the clamp interface and then lock the probe in place. Then, tighten the lower fixture gently so only the fiber is in the clamp face. The extra thickness of the Post-it Note provides for more positive clamping.

   Thanks to Mike Uptmor (TA Instruments) 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 FREE TA shirt and pen. Send your hints to rblaine@tainst.com.
Technical Information

Thermal / Rheology Installation Requirements Guide (Rev E)
The guide has been revised and updated to include all the Q Series™ thermal modules as well as our Rheometric Series rheometers. It will be especially useful to customers ordering new instruments, since it provides extensive information on weights, dimensions, electrical, gas, and laboratory bench space requirements. For the latest version of this valuable document contact info@tainst.com.

10th Anniversary of Modulated DSC®
This year marks the 10th anniversary of the introduction of Temperature Modulated DSC by Dr. Michael Reading. As has been well-documented by Dr. Reading and others, MDSC offers all the performance features of standard DSC, overcomes its limitations, and, in addition, provides advanced capabilities for separating the total heat flow signal into its heat capacity and kinetic-related component signals. The latter capability offers many significant advantages to thermal analysts, including a way of measuring the initial crystallinity of polymers, and the separation of overlapping thermal events (e.g., Tg and enthalpic relaxation events).

In the past decade, MDSC, as pioneered by Dr. Reading and TA Instruments, has survived both scientific and legal challenges, and is now an established technique. Its practical utility in solving material characterization problems has been well documented, both in textbooks, and in the hundreds of scientific papers presented at worldwide conferences. TA Instruments’ staff has conducted multiple worldwide seminars and workshops to educate our customers in the correct use and application of MDSC. Its current demand by thermal analysts is attested to by the fact that over 50% of the Q Series™ DSC systems shipped from our manufacturing facility contain MDSC.

In 2004, a definitive textbook on the theory and applications on MDSC will be published by Kluwar. Entitled The Characterization of Polymers by Modulated Temperature DSC®, it will be edited by Professor Douglas Hourston and Dr. Reading, and feature chapters on curing systems, blends, and semi-crystalline polymers by established experts in these important fields of study.

Use of the Photocalorimeter Accessory (PCA) with Tzero™ DSC
Photocalorimetry involves the introduction of UV / Visible irradiation of a sample while performing a DSC experiment. TA Instruments’ PCA has been developed utilizing Tzero Technology to offer several advancements over previous photocalorimetry devices, including the following: direct measurement and balancing of light intensity at the cell, dual sample capability, and the ability to provide MDSC® quasi-isothermal experiments in conjunction with the photocalorimeter experiment. Use the following link to access this applications brief (TA 305a).
Training Courses

Scheduled User Training Courses for ARES & RSA III

Get a Higher Level of experience with your ARES or RSA III

These are intensive two-day courses that combine lecture and hands-on training to give you the expertise that you need to run your rheometer and DMA. The courses consist of lectures on theory, calibration & maintenance, and hands-on sessions on setting up, running, and viewing/analyzing the data. Class size is limited to maximize the experience for the attendees, so register soon.

ARES classes are scheduled for Nov 18th & 19th, and Dec 16th & 17th
RSA III classes are scheduled for Dec 2nd & 3rd

For more information go to: www.tainst.com/support/trainingrheometrics.html

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Our On-site training courses are designed to give our customers the training they need, in the most efficient manner possible. These courses take place in your facility where you are trained on your equipment with your samples. We will customize a course for you that is lecture-based, hands-on, or a combination of both. A typical agenda for DSC might be as follows:

- DSC Theory & Instrumentation (Lecture)
- DSC Applications (Lecture)
- DSC Calibration & Maintenance (Hands-on)
- Running Your Samples (Hands-on)
- Analyzing Your Data (Hands-on)

Usually, we will cover one instrument per day, and the applications section will be geared towards your industry. The cost is just $1500 per day, plus travel expenses.

For more information contact training@tainstruments.com

Don't forget to check out our other training opportunities.
www.tainst.com/support/training.html
International Conferences and Exhibitions

International Congress on Rheology
For more information on the conference, or to register online, visit: http://www.icr2004.or.kr/home/index.asp

International Congress on Thermal Analysis and Calorimetry
Conference: September 12 - 19, 2004 – Chia Laguna, Sardinia, Italy.
For more information on the conference, or to register online, visit: http://www.ictac13.com/

For additional international conference and exhibits click the appropriate link below.

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More Information:  
germany@tainst.com  france@tainst.com  info@taeurope.co.uk  
spain@tainst.com  belgium@tainst.com  sweden@tainst.com  J-Marketing@tainstruments.com
New Staff at TA Instruments

TA Instruments is pleased to introduce **Bill Swartz** as Technical Representative for the Southern California territory. Bill joins TA Instruments with over 24 years of analytical instrumentation sales experience in the biotechnology, pharmaceutical, chemical, semiconductor and aerospace industries. Before joining TA Instruments, Bill was the western district sales manager for Rheometric Scientific.
Elmer — You’re NEVER going to catch up!!!!!
Connection between the new $20 Bill and TA Instruments
We are pleased to note that our AR 2000 Advanced Rheometer was used to define and characterize the complex inking system that appears in the new US $20 bill.

Web Updates
At TA Instruments, we are constantly attempting to keep our website attractive and useful to our customers and prospects. In our latest update, we have completely recast the information on the “Support” section, which includes service, training, applications library, technical support, and a parts and accessories price list. Visit it and browse the new information provided. We are always interested in your thoughts on how we can make our website increasingly useful.

New High Pressure DSC Pans
A new corrosion-resistant, high pressure DSC pan / lid has recently become available from the Swiss Institute of Safety & Security, which appears to be very promising for use with a variety of pressure sensitive materials. While TA Instruments does not endorse this product at this time, preliminary information from our customers indicates that it has capabilities and performance that merit serious consideration by thermal analysts who need such capabilities. The gold plated pans have the following specifications:

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<tr>
<td>Dimensions</td>
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<tr>
<td>Sealing pressure</td>
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<tr>
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Information and pricing on this product is available from the Swiss Institute of Safety & Security. Contact Dr. H. Fierz at 61-41-6965940 / e-mail: hans.fierz@swissi.ch
Synergy of the combined application of thermal analysis and rheology in monitoring and characterizing changing processes in materials

by A. Franck, W. Kunze, TA Instruments Germany

Keywords: synergy, thermosets, cure, DSC, MDSC, rheometer, viscosity, gel point, glass transition

SCOPE

Rheology and Thermal Analysis are important technologies used in material characterization and applied to performance and processing problem solving issues. Both techniques are extensively used in product formulation and development of new or modified products, and in the past these techniques were applied independently most of the time.

However for many applications and especially for monitoring and characterizing physical or chemical structure changes in materials, as shown in the following, the combined and targeted use of the two methods provides also synergy advantages.

INTRODUCTION

Chemical and physical processes in materials often go along with quite significant changes of the materials’ microscopic and/or molecular structure. Typical examples of chemical processes are the cross-linking of thermosets or the gelification of starch. Examples of physical processes, usually reversible, are the gelation of gelatin or the structure build-up in complex fluid systems including cosmetics, paints, slurries, etc..

Product quality and performance during processing or in the final application are not only dependent on the actual or final structure of the material, but also on the time dependent changes and the external conditions. Thermal Analysis and Rheology have become the most important characterization techniques because of their sensitivity to small changes in structure and the ease to monitor these structure changes. Recent developments of TA also have advanced considerably the frontiers in speed and accuracy of these techniques. [1]

APPLICATION EXAMPLE: THERMOSETS

Thermosets are solid materials, which result from cross-linking of multifunctional monomer units. The typical example are the Epoxy, Phenolic and Urethane based resins. The functionality of the monomers defines to a large extent the structure of the network. For a cross-linked system to form not just linear polymer chains, at least one of the educts

Figure 1 Schematical representation of the formation of a cross-linked network
has to be tri-functional. For example, cross-linked poly-urethane grows from a di-isocyanat and a triol.

In figure 1, the crosslinking reaction of a dimer and a trimer are shown schematically. An important physical quantity is the time, when a closed path over covalent bonds throughout the sample exists. At this point the steady viscosity becomes infinite – this point is referred to as gel point and depends predominantly from the chemical network structure.

A cross-linking reaction is typically monitored at constant temperature (isothermal) or at increasing temperature from a starting to a final value while recording the thermal and/or rheological parameters. As such, the viscosity decreases first with increasing temperature, then goes through a minimum as time and temperature advance to increase again, due to the extend of the cross-linking reaction. The viscosity of the resin during the reaction is an important parameter during manufacturing of carbon fiber reinforced composites for example. At the minimum, the viscosity has to be low enough to allow good wetting of the fibers and consequently provide a good adhesion of the fibres in the final product.

The location of the viscosity minimum in time is important and controls manufacturing parameters such as processing equipment settings. The heat flow, measured in a differential scanning calorimeter DSC under the same thermal conditions represents mainly the reaction heat of the cross-linking process. The reaction heat is a thermodynamic parameter and correlates to the conversion of the educts. Therefore, the measured heat flow represents the extend of reaction, or - how many monomer units have reacted under the given temperature conditions. (Figure 3)

A direct result of the cross-linking reaction for thermosets such as Epoxy- and Phenolic- resins, is a strong increase of the glass transition temperature. While the glass transition temperature of the educts is below the reaction i.e. test temperature, the glass transition, depending on the imposed temperature profile, may increase faster than the test temperature. As the glass transition temperature approaches the test temperature, the mobility of the growing network is significantly reduced. The reaction is now controlled by the diffusion of the reactive end groups and comes to a stop. The classic DSC measurement however cannot determine the change in the heat capacity, because the test signal is dominated by the heat of reaction. The modulated DSC (MDSC) however can detect the small change in the heat capacity. The MDSC modulates the temperature ramp with a small amplitude sinusoidal oscillation. These small variations in the temperature induce also small periodic variation of the measured
heat flow. The correlation of temperature and heat flow generates two heat flow signals, the reversing heat flow, which represents the heat capacity changes during the reaction and the non-reversing heat flow, which is a measure of all kinetic effects, as shown in figure 4. The glass transition is a reversible quantity and therefore shows up as a change of the heat capacity. The heat of reaction is non-reversible and therefore has no influence on the heat capacity.

With increasing temperature, the heat capacity signal increases as a result of the advancing crosslinking reaction. After reaching a maximum in the heat flow, the heat capacity signal decreases, due to the glass transition temperature approaching the test temperature - the sample changes from a rubbery to a glassy state – the reaction is now diffusion controlled. Since the test temperature increases continuously, the sample devitrifies and the heat capacity increases again, the reaction continues. The prove is the slow asymptotic fall of the reaction heat.

High performance composites, have to follow a well defined temperature profile in order to be able to reach the desired conversion level and the required strength. In order to determine the extend of reaction, the cured sample is subjected to a new DSC run. The post cure reaction hides the effect of the glass transition. (Figure 5). Again, only the MDSC is able to provide the desired glass transition temperature and the extend of the post curing.

The measurement of the heat flow or the heat capacity provides important information on the reaction, the reaction kinetics and the conversion. However, the thermal analysis does not provide any information about the structural changes at the molecular level. When probing the sample during the reaction with a small sinusoidal deformation, then the measured torque, after correlation with the input deformation, provides two quantities, the storage modulus G' or the stored (recoverable) mechanical energy and the loss modulus G'' or dissipated (non-recoverable) mechanical energy. The storage modulus and the mechanical loss tan δ (the ratio of G''/G') are characteristic for the changes of the material’s structure during cure [2]. According to Winter et al [3], G' and G'' as a function of frequency, follow a power law behavior at the gel point, in other words, the tan δ curves cross at the same time for all frequencies (Figure 6).

At the gel point, G' and G'' are proportional to the frequency to the power n

\[ G' \propto G'' \propto \omega^n \] [6].
The value of the exponent is approximately 0.5, if the stochiometry is equilibrated. In this case \( \tan \delta \) is approximately 1 at the gel point. This is the reason, why the cross over of \( G' \) and \( G'' \) can be used to determine the gel point according to figure 7.

Rheology and thermal analyses complement each other extremely well for measuring chemical changes in materials, such as the curing of thermosets. The DSC provides information on the extend of reaction and the conversion as a function of time, the rheology provides information about the structural changes, the gel point and also processing parameters in terms of the viscosity as a function of time. If the thermal and mechanical analysis have been performed with the same thermal history (temperature profile), the viscosity as a function of conversion can be easily calculated by variable transformation, as shown in figure 8 and the conversion at the gel point determined. This is an example of the synergy of the combined application thermal analysis and rheology for the characterization and monitoring of chemical processes in materials.

**CONCLUSION**

Thermal Analysis and Rheology are complementary analytical techniques for the characterization of chemical processes in materials, as shown for the crosslinking of thermosets. The combination of the two techniques is synergetic and thus provides additional information in regards to the structural changes and conversion during the crosslinking reaction.

**LITERATUR**

Limitations of DSC for the Measurement of Polymer Crystallinity

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INTRODUCTION
Differential Scanning Calorimetry (DSC) has been used to measure the crystallinity of polymers for over 40 years and is the most widely used technique in the polymer industry. However, results on semi-crystalline polymers and blends are often hard to interpret and typical analyses are often in error by as much as 50%.

A 1997 article by Y. P. Khanna and W. P. Kuhn titled Measurement of Crystalline Index in Nylons by DSC: Complexities and Recommendations summarizes the causes of the significant errors obtained by DSC on Nylon 6. It also describes how a combination of analytical techniques such as DSC, XRD and NMR, when combined with extensive experience, can be used to obtain more reliable crystallinity values.

The purpose of this paper is to illustrate the problems associated with measuring crystallinity by standard DSC and show how Modulated DSC® (MDSC®) overcomes them.

ILLUSTRATING THE PROBLEM
The data in Figure 1 is from a DSC experiment on Nylon 6/6. It shows a glass transition near 50°C followed immediately by cold crystallization. It is difficult to determine the size of the glass transition or the start of the crystallization peak because the transitions overlap. Using rather subjective integration limits, because there is no clear heat capacity baseline, results in a peak area of 21.9 J/g for crystallization. The region between 100 and 200°C appears to be a baseline region and there is a melting peak of 67.5 J/g. Subtracting the two areas results in an approximate crystallinity of 45.6 J/g.

Figure 2 is also a DSC experiment on the same sample of Nylon 6/6. However, the sample was heated to 150°C, cooled and reheated to 275°C. The second heat should be on a more crystalline sample which should have a lower heat capacity and less endothermic baseline. This is exactly what is seen up to 50°C, the glass transition temperature. Above 50°C, the first heat shows a more exothermic signal indicating that this is not a baseline but rather ongoing exothermic crystallization. Once the sample is heated above 150°C, the limit of the first heat, the signal again becomes more exothermic indicating further crystallization. This means that there is no heat capacity baseline between Tg and melting, and that it is not possible to integrate the crystallization and melting peaks or to measure the sample’s crystallinity.

Figure 3 is MDSC® data on the same Nylon 6/6 sample. Integration of the individual crystallization and melting peaks in the Total heat flow signal results in a calculated crystallinity of 45.6 J/g, the same as obtained by DSC. The MDSC® Nonreversing (kinetic) heat flow signal clearly shows that the sample is increasing in crystallinity from 50°C to 250°C. The Reversing heat flow signal shows that melting of the smaller, less perfect crystals begins near 150°C as compared to 200°C seen in the Total heat flow signal. The ongoing simultaneous crystallization makes it impossible to determine the true onset of melting in the Total heat flow signal.
MDSC® crystallinity is measured from the sum of the exothermic and endothermic processes seen in the Reversing and Nonreversing heat flow signals. The crystallinity of the sample is found to be 23.6 J/g, not 45.6 J/g as seen by DSC.

Figure 4 shows the Total heat flow signal from an MDSC® experiment. This signal is equivalent to that obtained by standard DSC at the same average heating rate. It shows Polybutylene Terephthalate (PBT) to have a crystallinity of about 44 J/g. The analysis of the data assumes that the region between 75 and 175°C is a heat capacity baseline and can be used for selecting integration limits.

Figure 5 shows the MDSC® analysis of polymer crystallinity for the PBT sample and provides a result of 19.3 J/g or only 44% of the value obtained by DSC. This large difference is the result of MDSC®’s ability to measure the increase in crystallinity that is occurring as the sample is heated (Nonreversing heat flow signal). Just as with the Nylon 6/6 sample, the exothermic crystallization process can be verified by heating the sample to specific temperatures in the range of the crystallization, cooling then reheating. At the annealing temperature of 75 and 125°C in Figure 6, the exothermic jump can be clearly seen in the second heat. It is also interesting to see how well the heat capacity baseline, just prior to the start of crystallization in the second heat, agrees with the heat capacity baseline of the MDSC® Reversing specific heat capacity (Cp) signal. Clearly, the sample is undergoing a significant increase in crystallinity as it is heated and it is not possible to measure its crystallinity by DSC.

CONCLUSION

The DSC measurement of polymer crystallinity can have errors in excess of 50% due to the fact that the crystallinity of the sample is increasing as it is heated and the operator is not able to select proper integration limits or determine the actual heat capacity baseline.

![Figure 1: Nylon 6/6 with DSC at 10°C/min.](image)
Figure 2: Annealing during DSC experiment.

Figure 3: MDSC® of Nylon 6/6.
Figure 4: Polybutylene terephthalate (PBT) crystallinity by DSC.

Initial Crystallinity = 109.1 + (-89.8) = 19.3 J/g

Figure 5: Accurate crystallinity of polybutylene terephthalate (PBT).
**Figure 6**: DSC/MDSC® overlay for polybutylene terephthalate (PBT).

**REFERENCES**

DSC Methods to Quantify Physical Aging and Mobility in Amorphous Systems: Assessing Molecular Mobility

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ABSTRACT
The specific heat capacity (Cp) of amorphous sucrose was determined by DSC after annealing at a particular temperature within the glass transition (Tg) region. The enthalpy recovery after physical aging was obtained from the Cp data through the Tg region after several aging times. This data was fitted to the empirical Williams-Watts equation to obtain values for the mean molecular relaxation time and a parameter for the distribution of relaxation times at the annealing temperature.

INTRODUCTION
Materials that have been melted then cooled under conditions where they do not crystallize exist in a super-cooled liquid state. They are amorphous—lacking in crystalline order—and their viscosity increases, and molecular mobility and specific heat capacity decrease, in a complex way as the material is cooled. These data exhibit an S-shaped curve when measured against temperature. The inflection or midpoint of the S is called the glass transition temperature (Tg). The measured value of Tg and the value of these parameters through the Tg region depend on the thermal history of the material. Slow cooling through the Tg region allows adjacent molecules to find configurations of low enthalpy with less excess volume from inefficient packing. Rapid cooling through the Tg region leaves the material in a metastable state with more voids and less favorable intermolecular interactions. This is often illustrated by a diagram showing relative enthalpy of the material as a function of temperature as it is cooled at rapid or slow rates from the melt. See Figure 1. Viewed in this way the Tg as defined by the enthalpy data decreases as the cooling rate decreases. This relative enthalpy diagram can be generated from DSC data by integrating Cp or heat flow data, as described in the appendix.

When a material has been cooled rapidly from the melt and is therefore in a higher enthalpy state it will “relax” into a lower enthalpy state when it is held isothermally within the Tg region. This exothermic process is represented in Figure 1 as a vertical arrow at the annealing (or “physical aging”) temperature, $T_{\text{iso}}$.
If the molecular mobility is sufficiently great at the selected temperature this process can be observed directly by isothermal DSC. This study focused on aging well below Tg where aging is too slow to observe directly.

The extent of physical aging (the length of the vertical arrow in Figure 1) depends on how long the material is held at this temperature, and on the mobility of the molecules to rearrange at that temperature. A material that has been aged at this temperature, then cooled to the DSC starting temperature will, when reheated, exhibit an endothermic peak in the Tg region. The difference in the area (enthalpy) between two DSC curves from samples having the same cooling history, but different aging times, is due to the “recovery” of the physical aging enthalpy. This method of assessing the mobility at the aging temperature calls for measuring the recovery of physical aging enthalpy after holding the sample for several aging periods. The extent of physical aging (the fraction of the total possible at that temperature) recovery is fitted to the Williams Watt equation to obtain the mobility parameters. (1)

**EXPERIMENTAL**

A Q1000™ DSC from TA Instruments was used to obtain specific heat data on amorphous sucrose. Because it uses proprietary Advanced Tzero™ Technology, the instrument calibration provides an internal compensation for the effects of DSC cell asymmetry. (2) The result is a baseline very close to zero milliwatts and a displacement from that baseline that is due almost entirely to the specific heat of the sample specimen itself. Hence, the DSC output from a single run can be accurately presented directly in Cp units.

The crystalline sucrose sample was heated above the melting point then removed and cooled in seconds to room temperature, thus trapping the sucrose in the amorphous state. The sample was reloaded in the DSC, equilibrated and heated over the temperature range to obtain Cp. Figure 2 shows the Cp data of several DSC runs in specific heat units after aging for various lengths of time.

Alternatively, this procedure can be carried out using normalized heat flow data; however, it is essential that there be no instrumental curvature in the baseline.

![Figure 2](image-url)

**Figure 2.** Specific heat capacity of amorphous sucrose after aging at Tiso for several periods. Difference in ΔH between these runs is due to differences in physical aging. (Individual areas have no physical significance.)
CALCULATIONS

To determine the differences in physical aging from different aging times the data was integrated over an identical temperature range. The physical aging enthalpy was taken as this integral (the area between the curve and linear baseline) for a run after aging, less that for a DSC run after no aging period. The extent of physical aging was obtained by taking this value and normalizing by the ΔH corresponding in Figure 1 to a vertical arrow between the un-aged run and the dashed line, which is an extrapolation of the enthalpy data of the equilibrium liquid. As shown in Figure 3, this is the ΔH corresponding to the area of the trapezoid defined by the heat capacity constructs below and above Tg and the verticals representing two fictive temperatures, that of the amorphous sample without physical aging, and that of one where the fictive temperature has moved all the way down to the temperature of physical aging, Tiso.  The fictive temperature, which is an uncommonly used definition for Tg is based on the intersection of pre- and post- transition lines on the enthalpy plot. It can also be obtained from DSC data as the temperature for which the area under the curve equals the area under the step function as indicated in Figure 3.

The extent of physical aging is the defined as:

\[ \phi = 1 - \left( \frac{\Delta H_t}{\Delta H_\infty} \right) \]  

Where:
\( \Delta H_t \) is the physical aging enthalpy
\( \Delta H_\infty \) is the total possible heat of aging.

The Williams-Watt relationship is: (1)

\[ \phi = \exp \left( \frac{t}{\tau} \right)^\beta \]  

Where:
\( t \) is the isothermal aging time at Tiso
\( \tau \) is the mean molecular relaxation time
\( \beta \) is a distribution figure for relaxation times

Figure 3. Determination of the total possible heat of aging, \( \Delta H_\infty \), at Tiso
RESULTS

To determine $\tau$ the data was fit by linear regression to the equation:

$$-\ln(\phi)^{-\beta} = \left( \frac{t}{\tau} \right)$$

Equation 3

The results of the fit are plotted in Figure 4. First, the value of $\beta$ was obtained by trial and error to produce a linear fit. This produced a value of $\beta$ of 0.3 +/-0.1. Then the inverse slope was calculated to obtain a mean relaxation time, $\tau$, finding a value of 11000 hours or 1.25 years, a value in reasonable agreement with previous data. (3)

DISCUSSION

The use of the Williams-Watts equation implies a particular model of viscoelastic behavior. Other empirical relationships may be used to relate molecular mobility to viscoelastic or, in this case, thermodynamic data.

The significance of these mobility parameters is that the mean relaxation time is the half-life with respect to the relaxation process that builds enthalpy when an amorphous material is held within the Tg region. (In this case, the Tg region extends down to the neighborhood of the Kauzmann Temperature where the extrapolated properties, specifically the entropy, of the super-cooled liquid equals that of the crystalline solid.) The process in question is that associated with the glass transition, which is primarily associated with the freezing-out, or melting, of molecular translation. Hence, determining $\tau$ should correlate with the half-life with respect to the interaction of molecular species in an amorphous matrix. It has been reported that this parameter does correlate with the shelf life of unstable pharmaceuticals in freeze-dried (amorphous) formulations. (3)

One consideration for this method is that to obtain usefully accurate values of $\tau$ requires carrying out physical aging experiments up to a few percent (at least) of the expected $\tau$ value. Thus, to predict the value of a shelf life of a year would require
holding the sample for several days (preferably weeks) at the proposed storage temperature. For this study, which was undertaken to draw attention to this method, the aging was carried out in the DSC cell. Thus, the collecting of long-duration aging was skimped on, to say the least. For this study aging was carried out at one temperature, but for unknown amorphous mixtures it would be preferable to carry out experiments at several aging temperatures. Of course, the value of $\tau$ would be different at each temperature, but both $\tau$ and $\beta$ would be expected to fall on a smooth curve with respect to temperature, and $\beta$ would be expected to vary only slowly with temperature. The data in this case was obtained on a single specimen of sample, and the sample was left in the DSC for the duration of data collection. Where multiple samples are analyzed and aging is carried out in a separate, thermostatted device, one should prevent moisture uptake by the sample.

Finally, this analysis is one requiring high sensitivity, accuracy and extremely reproducible instrumental baselines. The largest possible sample specimen should be used, and sample encapsulation and positioning in the DSC cell should be optimal and reproducible. The use of the Q1000 or Q100 with an autosampler is strongly recommended when multiple samples are to be analyzed and data combined.

REFERENCES
4. Tzero, Q1000 and Q100 are trademarks of TA Instruments

KEY WORDS
DSC, pharmaceuticals, molecular mobility, physical aging
How Tzero™ Technology Improves DSC Performance
Part VI: Simplifying Temperature Calibration for Cooling Experiments

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ABSTRACT

Because of thermal lag between DSC sample and temperature control sensors, most DSC’s require calibration at the heating rate to be used. Alternatively, calibration at multiple rates is required to correct for the heating rate dependence of thermal lag. Without this calibration there is considerable error in the temperature data in going from one heating rate to another. This problem is especially troublesome when performing a cooling experiment due to the thermal lag being in the opposite direct as that of heating doubling its effect. This problem is solved with a new DSC sensor employing Tzero™ technology. With the Q Series™ DSC system an additional thermocouple on the DSC sensor allows complete calibration of the DSC cell and compensation for all thermal lags, including those caused by the encapsulated sample. The use of a liquid crystal sample is described to demonstrate that the calibration is independent of heating or cooling rate, even when using a non-ideal hermetic sample encapsulation.

INTRODUCTION

Perhaps the most common DSC experiment performed is one using a heat-cool-heat temperature program. The first heating step gives information about the initial state of the sample “as received” and removes artifacts due to stresses caused by sample history or by specimen encapsulation. The cooling step quantifies the fusion, or gelation, characteristics, and puts the sample into a standardized state where it can be compared to other materials so treated. Then, the second heat allows the melting characteristics of the thermally defined specimen to be quantified.

One challenge with this approach is that the DSC is calibrated to give correct temperature data for the heating experiments. Unless a complex multiple rate calibration has been carried out using the appropriate experimental conditions (purge type, pan type and cooling system), there will be an error in the cooling run temperature readout of about two times the thermal lag. As discussed in a previous report (1), this thermal lag is proportional to heating rate, sample-plus-pan heat capacity and the thermal resistance between the sample specimen and the “sample temperature” sensor. The thermal lag is normally in the range of 0.4 to 0.9 • C (for 10 • /min), so if it has been corrected for the heating experiment (by DSC temperature calibration at the heating rate to be used for the samples), it is off by one to two Celsius degrees for the cooling data (2, 3).

This problem is eliminated using Advanced Tzero™ Technology from TA Instruments. The Q1000 DSC cell provides an additional thermocouple sensor and an automated calibration routine that allows all the thermal characteristics of the cell -- both
those affecting the ordinate baseline, and those affecting the temperature scale -- to be addressed (4).

But how can one verify that this problem has been eliminated even for cooling experiments, given that most common temperature calibration materials super-cool making them unsuitable for calibration on cooling. A suitable tool is the use of certain liquid crystalline materials that do not super-cool.

**EXPERIMENTAL**

The liquid crystal material used is \((+)-4\text{-n-hexyloxyphenyl} 4’-(2”methylbutyl)-biphenyl-4-carboxylate\), known as CE-3. This material was obtained in purified form from a commercial vender (5), the use of which is described in ASTM standard E2069 for DSC calibration on cooling (6). 1.5 milligrams of a purified sample of CE-3 was encapsulated in a hermetically sealed pan.

Figure 1 shows a thermal curve showing two-phase transitions of this material. Note that while the solidification of the sample into a solid shows considerable super-cooling, the onset of the higher temperature peak (just under 80 °C) appears at the same temperature. It is this transition that allows for a more carefully examination of the scanning-rate invariance of the Advanced Tzero temperature data.

The DSC used to demonstrate this was a Q1000 DSC from TA Instruments. The Advanced Tzero Technology capability comes standard with this model. This capability allows the thermal characteristics of the sample pan, as well as those of the DSC sensor itself, to be addressed in the output signals. This is accomplished using a cell calibration that does not require the use of any particular sample pan. Once calibrated, the system properly compensates for thermal lag caused by heat flow within the DSC sensor, and into the capsule containing the sample. As a result, one can consider that the temperature displayed on the X-axis is the *sample pan temperature*, the temperature at the surface of the sample specimen itself. This is a considerable improvement over reporting the temperature solely based on a sensor embedded in a DSC disk, sample holder, or yet farther removed from the sample (7). The Q1000 DSC was calibrated using only sapphire heat capacity standard scanning at 20 °C/min and indium metal for a melting standard, encapsulated in a standard aluminum pan. No special care was taken in calibration, or to “fine-tune” the instrument.
RESULTS

Figure 2 shows the results of heating and cooling the CE-3 system through a liquid crystal phase change transition. This peak corresponds to the transition between two liquid crystalline phases, the chiral smectic phase and the cholesteric phase. The correct transition temperature for this single valued point is obtained by extrapolating the peak onset back to the isothermal baseline, the zero heat capacity line (which on the Q Series is zero milliwatts). This can be seen to be 79.7 °C as measured either heating or cooling. Using the standard method of onset from the peak baseline gives a maximum temperature offset of 0.2 °C when using heating rates up to 30 °C/min or cooling rates up to 20 °C/min. Moreover, when using standard aluminum pans for encapsulation, this offset will be even less.

CONCLUSIONS

Some liquid crystal transitions are known to exhibit very little super-cooling. Therefore, the onset of this transition should appear at the same temperature as it is heated or cooled at normal DSC scanning rates. That this is demonstrated using the Q-Series DSC shows that the compensation provided by Advanced Tzero Technology is effectively addressing all thermal lag in the DSC/sample pan system. To make this proof even more convincing, the experiment was carried out in the less-than-ideally-coupled hermetic sample pans often used for the analysis of organic materials containing volatile components.

What does this mean for ordinary heat-cool-heat analysis, or any other routine cooling experiment? It means that for all practical purposes you can calibrate the DSC at any reasonable heating rate, and the DSC temperature data will be correct within a few tenths of a Celsius degree for data taken at other heating or cooling rates. Because advanced Tzero compensates for the effect of pan thermal mass and coupling, it is possible to calibrate using one pan type and then use another pan type (as was done in this report) without incurring substantial error. In short, because Tzero technology utilizes more information about the DSC itself in its measurement, it is safe to run under a wider range of conditions without calibrating under those specific conditions.

REFERENCES


5. 99.9% Purity from Chromophore, Inc., Huntsville, AL.


7. Some DSCs even report the sample temperature based on the output of a sensor in the furnace. Often, DSC manufacturers do not explain where the temperature signal is measured.

**KEYWORDS**

differential scanning calorimetry, organics