SII NanoTechnology Inc.

DSC AS PROBLEM-SOLVING TOOL: MEASUREMENT OF ENTHALPIC RELAXATION AT Tg

Problem

A scientist working for a pharmaceutical company wishes to have a straightforward means of assessing the effects of aging on the glass transition event (Tg) associated with their products. This information is useful for estimating the shelf life of a material and for quantifying age related problems.

Solution

Differential scanning calorimetry (DSC) provides an easy to use, yet sophisticated, means of studying the glass transition event and the effects of aging on Tg. DSC measures the heat flow into or out of a sample as it is either heated, cooled or maintained under isothermal conditions.

As an amorphous or glassy material is aged at temperatures below its Tg, the sample can develop a significant enthalpic relaxation peak which occurs in the vicinity of the glass transition event. The development of the enthalpic relaxation peak is due to the non-equilibrium nature of the glass transition event and is a consequence of the second and third laws of thermodynamics relating to the entropy of the material. The quantification of the area under the enthalpic relaxation peak gives valuable information on the aging time and/or temperature for an amorphous material.

One easy means of quantifying the change in enthalpy associated with the relaxation peak is through the application of a simple, cyclic DSC experiment. This entails heating the 'as received' or aged sample through its Tg, cooling back to the starting temperature, and then reheating at the same rate. The data from the reheat portion of the experiment is simply subtracted from the initial heating data to yield the irreversible or non-reversing data set. The entire cyclic experiment can be conducted at heating and cooling rates of 20°C/min which gives a short 'run time' and yet provides complete data.

It has been suggested that the only means of assessing the effects of aging at Tg is through the use of the approach known as temperature modulated DSC (TMDSC). The non-reversing signal generated by TMDSC yields the quantitative heat of enthalpic relaxation. However, standard, cyclic DSC also provides this information in a shorter overall time period. The maximum heating rate which can be used with TMDSC is 5°C/min as compared with 20°C/min with standard DSC. Over an experimental temperature range encompassing a glass transition event (120°C), the TMDSC approach

Thermal Analysis & Surface Solutions GmbH
Pfingstweide 21
61169 Friedberg - Germany

+49-6031-16223-1
+49-6031-16223-29
Info@thass.net
http://thass.net

would require a total time of 24 minutes. The cyclic DSC experiment performed at 20°C/min takes only 19 minutes and yields equivalent information.

In addition to the shorter experimental time, cyclic DSC offers the following advantages over TMDSC:

- the splitting of the TMDSC total heat flow signal into the reversing and non-reversing requires an extra calibration factor, KCp, which is dependent upon the given experimental conditions (periodicity, amplitude, heating rate)
- the TMDSC approach causes a experimentally related phase lag which must be accounted for accurately in order to obtain quantitative information. Standard DSC does not have a phase lag problem.

The Seiko EXSTAR DSC6200 offers the following major advantages for the study of the effects of aging at Tg:

- High sensitivity
- Very stable baseline performance for consistent, reproducible results
- Exceptional subambient performance for the study of Tg's near or below 0°C
- State-of-the-art, add-on robotics accessory for unattended operation
- 20-point temperature calibration for the greatest accuracy
- 10-point enthalpic calibration for accurate heat capacities and heats of transition

The effects of physical aging on the thermal properties of a cough drop were analyzed using the cyclic DSC approach. A cough drop contains a large amount of amorphous sucrose and the material undergoes physical aging as it sits on a shelf.

The following conditions were utilized to study the glass transition event, and its accompanying enthalpic relaxation, using the cyclic DSC approach:

Instrument:	Seiko DSC
Heating rate	20°C/min from -10 to 110°C
Cooling rate:	20°C/min from 110 to -10°C and hold 1 minute
Heating rate:	20°C/min from -10 to 110°C
Sample mass:	6.5 mg
Sample pan:	crimped aluminum pan
Purge gas:	nitrogen at a flow rate of 50 mL/min

Displayed in Figure 1 are the DSC results obtained from the heat-cool-reheat approach on the cough drop sample. The plot shows the

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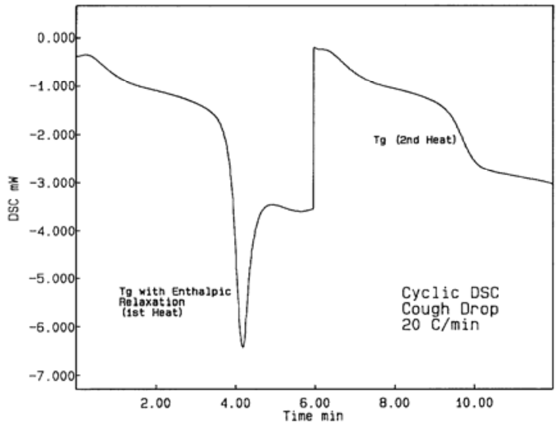

Figure 1

DSC heat flow as a function of time. During the first heating segment, a large enthalpic relaxation peak occurs in conjunction with Tg. When the sample is cooled and then reheated, a simple, stepwise change is obtained at Tg, and this data represents the reversible properties of the sample. To obtain the irreversible data set, the results generated during the second heat are subtracted from those of the first heat using the Seiko DSC-Subtraction software.

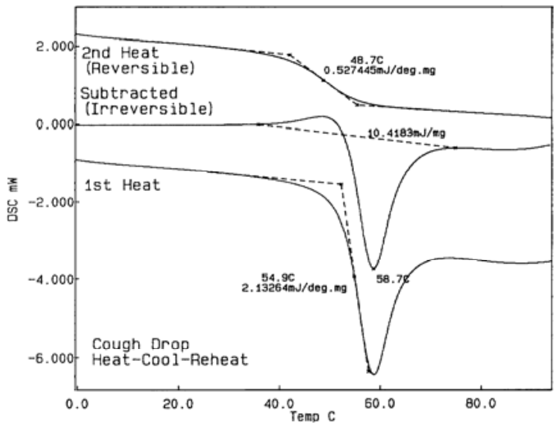

Figure 2

Displayed in Figure 2 are the three data sets obtained by cyclic DSC on the aged cough drop. The lower trace is that of the as-received sample and this shows the enthalpic relaxation peak in conjunction with Tg. The upper curve represents the reversible aspects of the sample and this shows the classic, stepwise change in the heat flow at Tg

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at 48.7°C. The center trace, or subtracted data, reflects the irreversible properties of the sample. The integration of the irreversible peak gives an accurate measurement of the enthalpic relaxation, which is related to the effective age of the sample. Longer aging times give rise to a larger enthalpic relaxation peak.

Summary

Cyclic DSC experiments can be performed on aged amorphous materials to quantify the enthalpic relaxation peak occurring at Tg. Since the cyclic experiments can be conducted at a rate of 20°C/min, this yields data in a shorter time span than temperature modulated DSC (TMDSC). Three data sets are generated from

the cyclic approach: as- received, reversible and irreversible. The integration of the peak obtained in the irreversible data set gives the accurate measurement of the enthalpic relaxation and this is related to the effective age of the sample.

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