SII NanoTechnology Inc.

DSC AS PROBLEM-SOLVING TOOL: HEAT CAPACITY MEASUREMENTS AND BETTER ASSIGNMENT OF Tg

Problem

A scientist developing a new polymeric material is having difficulty in identifying the glass transition temperature. The DSC shows a large endothermic melting transition, but not a well defined Tg. Shown in Figure 1 are the DSC heat flow results obtained on the polyolefin sample and it is difficult to decide on the assignment of Tg from this data.

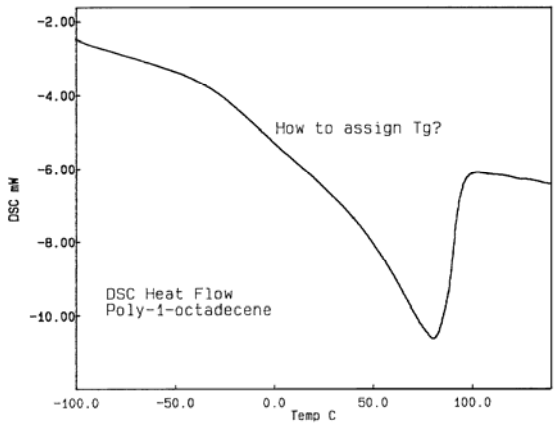

Figure 1

Solution

Heat capacity measurements (Cp) can provide for a better assessment of the glass transition event since the data is more quantitative than standard DSC heat flow. The heat flow can be affected by baseline curvature and other

instrumental factors. Many of the instrument effects are eliminated through the measurement of sample Cp.

The Seiko DSC system provides an accurate, precise and easy-to-use means of measuring the sample's heat capacity over a wide temperature range. The Seiko DSC offers:

- high sensitivity
- stable baseline performance
- excellent subambient response

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These factors are critical when attempting to accurately measure heat capacity values.

When performing heat capacity measurements, three experiments are performed:

- baseline run (empty DSC cell)
- sapphire run
- sample run

All three experiments must be conducted under identical conditions (i.e., heating rate, starting and ending temperatures).

The following guidelines will provide the best possible Cp measurements on samples:

- Ensure that the DSC has been calibrated for temperature and enthalpic response using high purity metal indium
- Best results are obtained on solids
- When analyzing powders, compress the powders into the pan with a glass rod
- Use a sample mass of 15 to 30 mg for most polymeric materials (samples with a low heat capacity may require a greater mass for better results)
- The mass of sapphire standard should be 30 to 40 mg
- Weigh the sample and sapphire to a precision level of 0.01 mg
- Use a crimped aluminum pan for solids
- After crimping, ensure that the bottom of the pan is flat and not rounded
- The mass of the sample and reference pans should be within ±0.05 mg of each other
- Heat at a rate of 20 or 10°C/min
- Start at a temperature which is about 40°C below the temperature of interest
- Hold isothermally at the starting temperature for 3 minutes
- Use a nitrogen purge at a flow rate of 50 to 100 mL/min
- The sample should not lose weight during heating (more than 2%)
- Do not 'zero-out' the DSC heat flow by depressing the zero key
- Run the baseline experiment first
- Run the sapphire experiment second
- Run the sample last
- Subtract the baseline run from the sample and the sapphire using the DSC Subtraction software and save subtracted files
- Analyze the subtracted sample and sapphire standard files with the DSC Cp software

Displayed in Figure 2 is an overlay of the DSC results obtained on a baseline experiment, sapphire, and sample when heated at a rate of 10°C/min from -100 to 150°C. These three data files permit the accurate assessment of the sample's Cp using the DSC Subtraction and DSC Cp software.

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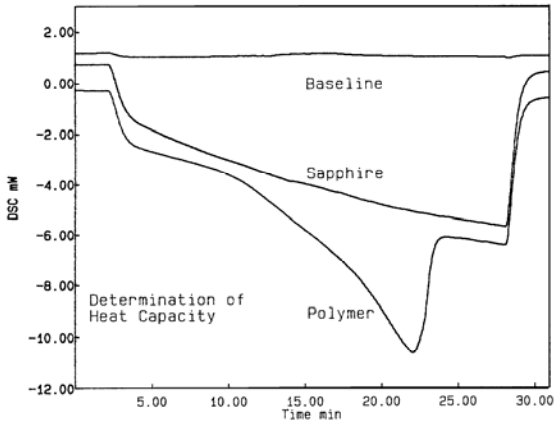

Figure 2

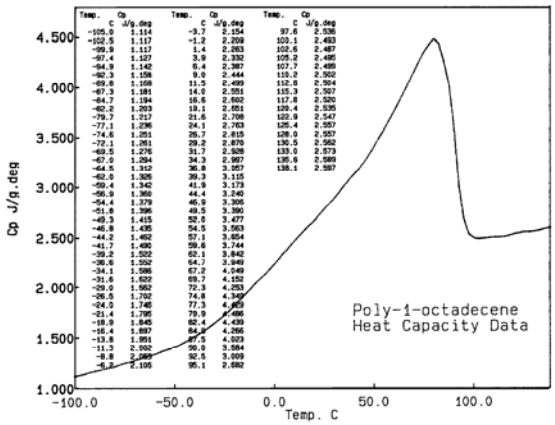

Figure 3

The determination of the heat capacity data can permit a better assignment of Tg, for many materials. Shown in Figure 3 is the quantitative Cp data for the polyolefin material.

The liquid heat capacity data obtained in the region above the melting endotherm can be linearly extrapolated to lower temperatures and all known polymers exhibit linear Cp response down to 150°K (-123°C). The liquid heat capacity data thus provides an excellent, thermodynamic means of helping to assign a sample's glass transition event.

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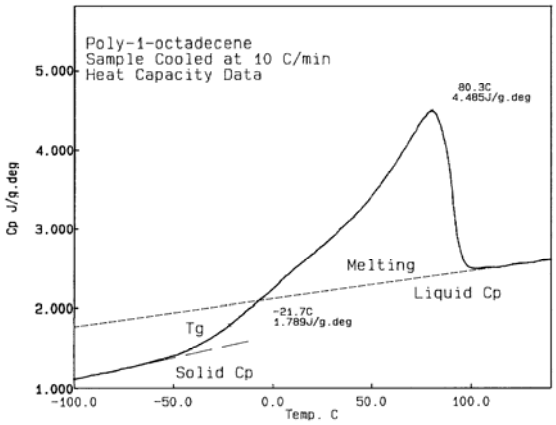

Figure 4

Displayed in Figure 4 is the sample heat capacity data now showing the extrapolated liquid and solid heat capacity data. The Tg must be between these two heat capacity responses, since Tg for an amorphous material is the mid-point between the solid and liquid heat capacities. For the polyolefin material, the mid-point temperature is -21.7°C and this represents the best-guess assignment of Tg for this material. The sample's true Tg may be slightly different from -21.7°C since the material is semi-crystalline rather than totally amorphous. The polyolefin sample apparently passes through its Tg at -21.7°C and then immediately begins melting. The melting transition is broad because of variable ethylene main chain segment lengths.

As a final note, the technique known as temperature modulated DSC (TMDSC) would not apply in the identification of the Tg of this sample since the sample undergoes melting immediately above its Tg. Because of severe instrumental phase lag problems, which take place in the melting regions, TMDSC yields indecipherable and erroneous data making data interpretation more, rather than less, difficult.

Summary

Heat capacity measurements can be easily performed on the Seiko DSC system with a high degree of accuracy and precision. The liquid Cp data obtained above a sample's melting point can be linearly extrapolated to lower temperatures to provide for a better measure of the glass transition event.

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