SII NanoTechnology Inc.

DSC AS PROBLEM-SOLVING TOOL: BETTER INTERPRETATION OF Tg USING CYCLIC DSC

Problem

A scientist is having difficulty in interpreting DSC results on a sample of polystyrene film. The sample exhibits a complex heat flow response in the vicinity of Tg complicating the interpretation of the results as shown in Figure 1. The scientist would like a efficient means of characterizing the sample in order to provide the most meaningful data and a clear identification of the glass transition event (Tg).

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.

The glass transition event, as measured by DSC, can sometimes be difficult to clearly identify or to characterize. This is due to the fact that Tg is a non-equilibrium event and time (i.e., aging time, heating rate, cooling rate), thermal history and other factors can have a major influence on the glass transition temperature, the magnitude of the heat capacity change at Tg, and the overall shape of the event. The non-equilibrium nature of Tg coupled with the manifestations of the second and third laws of thermodynamics, with respect to the entropy of the material, can make the interpretation of the DSC results at Tg somewhat difficult.

One easy means of better understanding the glass transition event is through the application of a simple, cyclic DSC experiment. This entails heating the 'as received' 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 irreversible effects at Tg (such as enthalpic relaxation due to physical aging) is through the use of the approach known as temperature modulated DSC (TMDSC). The non-reversing signal generated by TMDSC yields the irreversible aspects occurring at Tg. However, standard, cyclic DSC also provides this information in a shorter overall time period. The maximum heating

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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 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

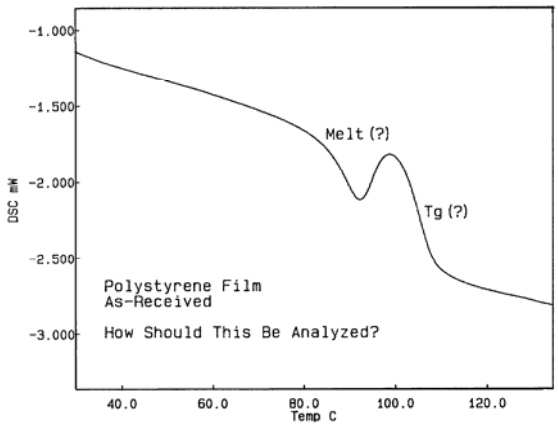

Figure 1

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Displayed in Figure 1 are the DSC results obtained on a polystyrene film using a heating rate of 20°C/min. The interpretation of the data for this particular film is not straight-forward. The sample appears to have an endothermic/exothermic response in the vicinity of Tg and this makes the clear identification of Tg difficult and ambiguous.

Cyclic DSC can be used to make the understanding of the events occurring at the glass transition for this particular sample much easier.

The following conditions were utilized to study the glass transition event using the cyclic DSC approach:

Instrument: Seiko DSC6200
Heating rate: 20°C/min from 10 to 155°C
Cooling rate: 20°C/min from 155 to 10°C and hold 1 minute
Heating rate: 20°C/min from 10 to 155°C
Sample mass: 7.3 mg
Sample pan: crimped aluminum pan
Purge gas: nitrogen at a flow rate of 50 mL/min

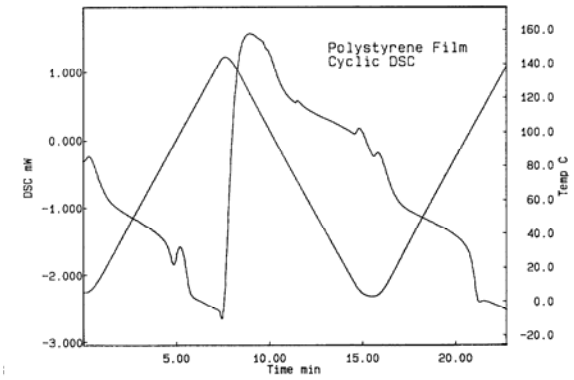

Figure 2

Shown in Figure 2 is the complete cyclic DSC data (heat-cool-reheat) obtained on the polystyrene film specimen. The total time of the experiment is 23 minutes (versus 29 minutes that would be required to perform an equivalent TMDSC experiment).

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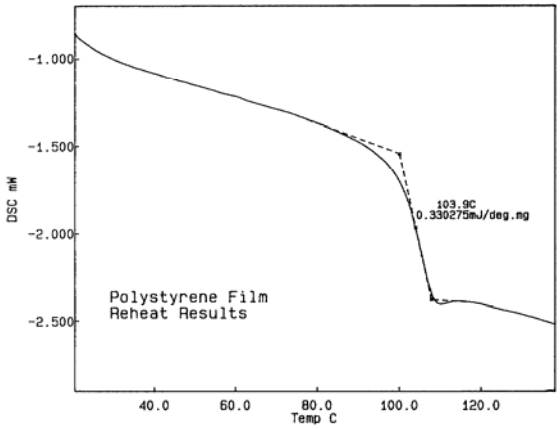

Figure 3

The results of the second heating segment are displayed in Figure 3 for the polystyrene film. A well-defined, and easily interpretable, Tg is obtained during the reheat portion. This data reflects the reversible aspects of the glass transition event for the sample.

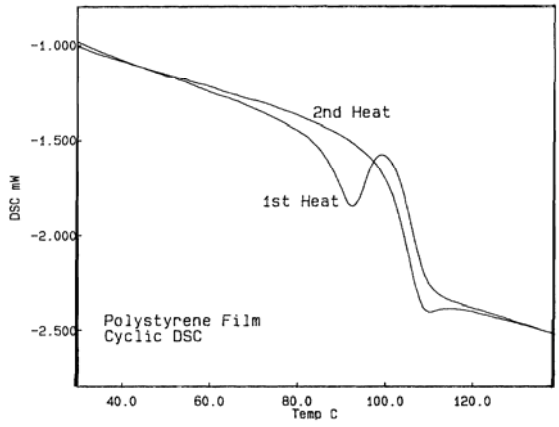

Figure 4

Shown in Figure 4 is a direct overlay of the DSC results obtained during the first and second heating segments for the polystyrene film. The effects due to sample processing and thermal history are evident on these results. The sample had been prepared under pressure and strain was frozen into the material during cooling. As the as-received film is heated in the DSC, this frozen-in strain is relieved which manifests itself as endothermic and exothermic behavior in the vicinity of Tg.

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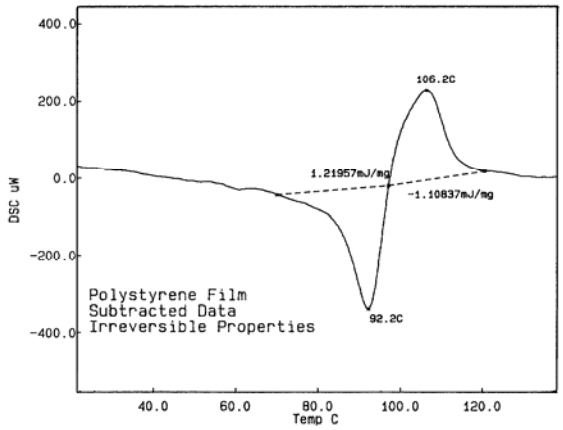

Figure 5

The DSC results obtained during the second heating segment (reversible) can be subtracted from the first heating portion to yield data which reflects the irreversible aspects of the sample response near Tg. The subtracted or irreversible data file is displayed in Figure 5 for the polystyrene specimen. It may be seen that the sample yields both endothermic and exothermic responses in the vicinity of Tg due to the effects of strain release.

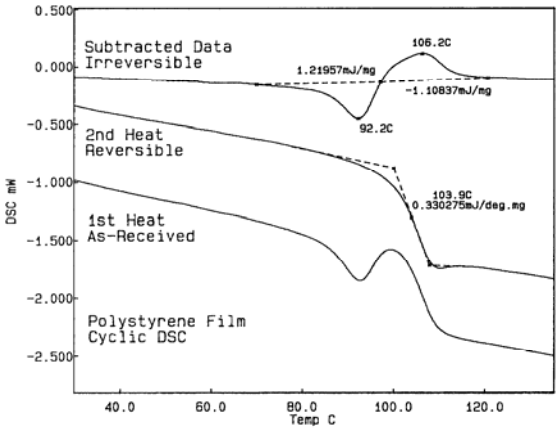

Figure 6

All three data sets obtained for the polystyrene film using cyclic DSC are displayed in Figure 6. The lower most curve represents the first heat or as-received results. The center set of results reflects the reversible aspects of the glass transition event for the polystyrene film and shows a well-defined, step change in the heat flow at 103.9°C. The

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upper most curve represents the irreversible aspects of the glass transition event associated with this particular polystyrene film sample.

Summary

Cyclic DSC experiments can be performed on amorphous materials to quantify the irreversible effects occurring at Tg, such as strain release or enthalpic relaxation. 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. This information greatly aids in the interpretation of the glass transition event of the 'as-received' sample.

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