Enhanced Characterization of Nylon Using Stepscan DSC

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Problem

A researcher at a polymer R&D center has a need to easily measure the glass transition temperature of ambient exposed nylon 6 fibers for the development of carpet yarns. The problem is that the Tg is masked by the evolution of absorbed moisture as the DSC heats the nylon fibers. The researcher desires an alternative approach to DSC for the measurement of the Tg of the 'wet' nylon fibers.

Solution

In its continuation of developing innovative thermal analysis products, PerkinElmer is introducing a new software package, StepScan DSC, for the enhanced characterization of the thermal properties of materials. The method is straightforward and utilizes the traditional approach for measuring the heat capacity, Cp, for the highest possible reliability of results without interfering experimental problems. The StepScan DSC approach is only possible with the design of the power compensated Pyris 1 DSC, with its very low mass sample and reference furnaces and rapid response time.

Figure 1 shows the StepScan DSC approach with the application of a repetitive sequence of short heat-hold segments.

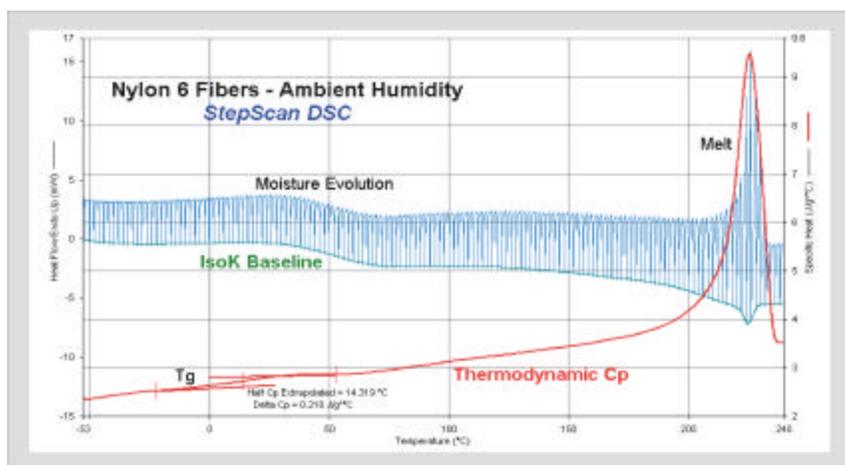*Figure 1. StepScan DSC Data Showing Repetitive Heat-Hold Segments.*
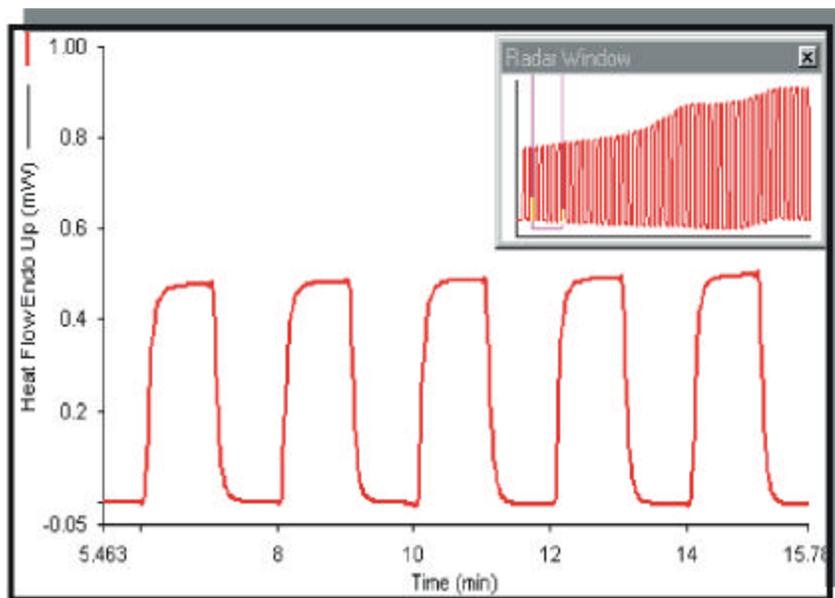
With the application of heating over small temperature increments (2°C), and by holding for a short time interval (e.g., 30 seconds), the heat capacity that is yielded reflects the reversible aspects of the sample. Kinetic or irreversible effects (on the time scale of the experiment) are eliminated in the **Thermodynamic Cp** data set. For example, if a sample has a glass transition, Tg, which has an overlapping enthalpic relaxation, moisture loss or crystallization event, the Thermodynamic Cp signal will show the classic, stepwise change in the heat capacity, which makes it simple and straightforward to analyze and interpret. The StepScan DSC approach also provides the kinetic or **IsoK Baseline** data set, which is reflective of the irreversible or slow processes taking place during the experiment. The enthalpic relaxation event, which can occur on physically aged samples at Tg, will show up in the IsoK Baseline data set.

Because the StepScan DSC approach requires rapid response, the technique is only feasible with the power compensated DSC, which allows for fast heating and thermal

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instruments.

Figure 2. StepScan DSC Results on Nylon 6 Fibers Exposed to Ambient Humidity.

Instrument:	Power compensated Pyris 1 DSC
Mode:	StepScan DSC
Heating rate between steps:	10 C/min
Isothermal hold time:	0.4 min
Temperature increment:	2 C
Sample mass:	Approximately 10 mg
Sample pan:	Crimped aluminum pan with hole in lid

DSC approach with the following experimental conditions:

equilibration. The application of the StepScan approach to a large mass furnace, heat flux DSC instrument would be difficult or technically unfeasible due to the inability to rapidly respond and equilibrate.

The other advantage of the StepScan DSC approach is that it provides a direct heat capacity measurement using the traditional and time-proven means without the need for deconvolution or the extraction of sine wave amplitudes. Other techniques, such as TMDSC (temperature modulated DSC), as applied to a large mass, heat flux furnace, oftentimes have problems due to distorted sine waves and phase lag. Because of the direct nature of the StepScan DSC experimental approach for assessing the thermodynamic heat capacities, the results are not plagued with these experimental difficulties.

StepScan DSC Results on Nylon 6

As an example of the ability of StepScan DSC to provide enhanced characterization information on materials, a sample of nylon 6 fiber was analyzed. Nylon fibers can readily absorb moisture, because of their high surface area and the hydrophilic nature of nylon itself. The glass transition event associated with nylon is plasticized due to the presence of the absorbed moisture and can vary by approximately 80 C depending on the moisture content.

With standard DSC, the nylon will simultaneously evolved moisture and yield its Tg near 20 C. The evolution of moisture is observed as a large endothermic peak, which masks the plasticized Tg. The StepScan DSC approach separates out the reversible (Tg) and kinetic (moisture evolution) events thus providing a clear identification of the plasticized Tg of the nylon.

A textured nylon 6 fiber sample was analyzed using the StepScan

The nylon 6 fiber was analyzed in three moisture-related configurations:

- Exposed to ambient moisture
- Saturated (100% moisture absorption)
- Dry (no absorbed moisture)

Displayed in Figure 2 are the StepScan DSC results generated on the ambient exposed nylon 6 fibers.

The plot shows the raw StepScan DSC data (blue curve), the Thermodynamic Cp data set (red) and the IsoK Baseline response (green). The DSC results show that the absorbed moisture evolution peak at 20 C occurs simultaneously with the plasticized Tg. Using the Thermodynamic Cp data set, the plasticized glass transition event is clearly observed at 14.3 C. The StepScan DSC approach makes it possible to easily detect the Tg of the 'wet' nylon 6 fibers.

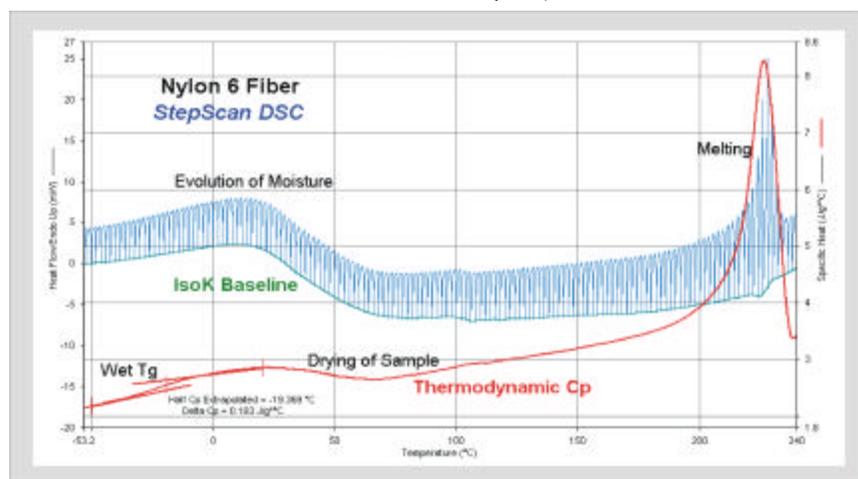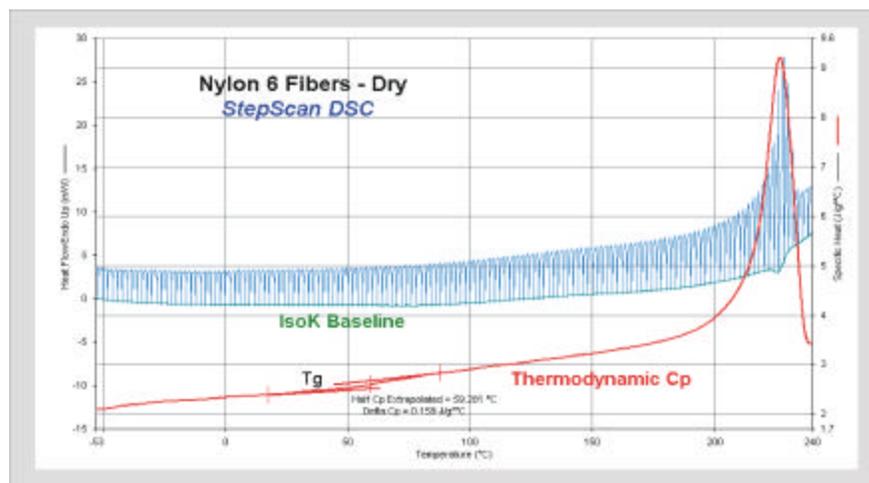A sample of the nylon 6 fibers was exposed to 100% moisture saturation in order to provide the maximum

Figure 4. StepScan DSC Results on Dried Sample of Nylon 6 Fibers.

moisture absorption. The StepScan DSC results from the completely wet nylon 6 fibers are displayed in Figure 3.

These results show that the moisture evolution peak, in the IsoK Baseline data set, is much more pronounced than for the nylon sample exposed to ambient humidity conditions. The Thermodynamic Cp data set shows that the Tg of the completely wet nylon 6 fibers has dropped to –19.4 C, due to the plasticizing effects of the high level of absorbed moisture. As the sample is heated above room temperature, significant drying occurs and the sample heat capacity

decreases as a result of the drying effects.

A sample of the nylon 6 fibers was dried prior to the analysis in order to eliminate all absorbed moisture content. The StepScan DSC results generated on the dry nylon 6 fibers are shown in Figure 4.

The IsoK Baseline response shows no evidence of the moisture evolution endothermic peak reflecting that the fiber sample is completely dry. The Thermodynamic Cp results reveals that the Tg of the completely dry and unplasticized nylon 6 fibers occurs at 59.3 C.

The StepScan DSC results provide for the completely separation of the reversible (Tg) and kinetic (moisture evolution) thermal events occurring as the nylon 6 samples are heated. The Thermodynamic Cp component provides for the clear and unambiguous assignment of the plasticized Tg of the wet nylon samples. The Tg ranges from –19.4 C for the completely wet nylon fibers to 59.3 C for the completely dry nylon fibers.

The StepScan DSC results demonstrate that the physical properties of nylon 6 change quite significantly with regards to moisture content. This means that a component or part manufactured from nylon would need to take into account the moisture of the ambient air under the operating or end-use conditions.

Summary

StepScan DSC provides a useful means for the enhanced characterization of the thermal properties of samples. The technique uses a series of heat-hold steps, which

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encompass the temperature range of interest. The StepScan DSC results provide the *Thermodynamic Cp* or reversible heat capacity signal along with the kinetic or *IsoK Baseline* data set. The use of StepScan DSC helps in the clearer interpretation of transitions (e.g., Tg) which may be masked or obscured with interfering irreversible events, such as enthalpic relaxation, stress relief, moisture evolution, crystallization, curing, etc.

StepScan DSC requires a DSC instrument with very high resolution and responsiveness and is feasible only with the power compensation Pyris 1 DSC. The StepScan DSC approach offers the following advantages over other methods, such as TMDSC:

- Direct measurement of thermodynamic Cp (no deconvolution required)
- Straightforward
- Free of experimental problems such as gradients, sine wave distortions or phase lag
- Accurate
- Hassle-free

The StepScan DSC approach offers similarities to TMDSC in that the long term and short-term thermal events can be separated. But StepScan DSC is different in that no deconvolution or Fourier transform is required thus eliminating many potential experimental problems.