Thermal Analyzer Differential Scanning Calorimeter NEXTA® DSC Series

Shinya Nishimura

1. Introduction

Differential scanning calorimetry (DSC) is a method of thermal analysis that allows observation of various physical transitions in materials—including melting and fusion, glass transition, crystallization, and thermosetting—as well as measurement of physical properties such as the specific heat and purity from analysis of the thermal history. These capabilities make DSC an essential tool for analyzing the thermal behavior of materials, and the technique is widely used both in Japan and around the world for research, development, and quality control in fields such as polymeric materials, inorganic materials, pharmaceuticals, and petroleum chemistry.

Since the 1970s, Hitachi High-Tech has been developing proprietary heat-flux DSC systems and marketing them around the world. In 2020, Hitachi High-Tech released two instruments in its NEXTA DSC series of next-generation thermal analyzers: the standard-model DSC200 system and the high-end DSC600 system.

Fig. 1 The DSC600 differential scanning calorimeter thermal analysis system.

2. Overview of the NEXTA® DSC Series

In recent years, the growing trends toward hybridization and high functionality of materials and material constituents have created increasingly diverse, increasingly complex demands for thermal analyzers capable of characterizing the thermal properties of materials—and, specifically, how the functional properties and effects of various materials vary with changing temperature—from researchers in many fields of science and engineering, from basic research to product development. Defect analysis for electronic products—which are constantly increasing in performance while shrinking in size—requires analyzing, and identifying the constituents of, minuscule samples containing only trace quantities of materials. This demands high-sensitivity instruments capable of high-precision measurements and high baseline performance to enable stable, reproducible measurements. High baseline performance is also a key prerequisite for accurately measuring the thermal properties of polymers, including the highly-functional polymer materials and films used in the automobile and aerospace industries and many other fields.

The NEXTA® DSC series of instruments offers three key features to meet these challenging market needs: (1) high measurement sensitivity, (2) stable baseline reproducibility, and (3) the Real View unit for observing samples at low temperatures.

3. High Measurement Sensitivity

The basic temperature sensor used to detect differential heat signals in DSC measurements is the *thermocouple*. Multiple thermocouples may be connected in series to yield a compound detector known as a *thermopile*. The NEXTA® DSC600 features a proprietary Hitachi-developed thermopile DSC sensor capable of high-precision measurements with a sensitivity below 0.1 µW, enabling accurate measurements of challenging samples such as blended resin materials or trace quantities of additives within parent materials.

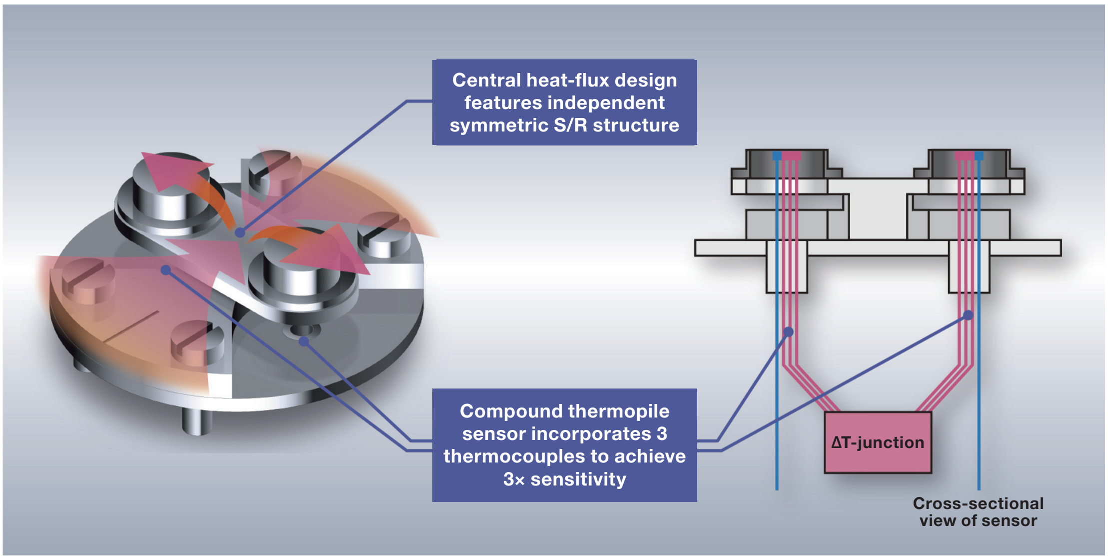

Fig. 2 Structure of the DSC sensor in the DSC600 system

The high measurement sensitivity of the DSC600 is demonstrated by an application case study involving high-sensitivity measurements of a carbon-fiber-reinforced epoxy resin used as a structural material for automobiles and aircraft. This material is an epoxy resin produced by adding carbon fibers to a resin material for increased mechanical strength. Because the resin fraction of the resulting material is lower than that of pure epoxy resin, accurate detection of its glass transition and exothermic peaks requires high measurement sensitivity and baseline stability.

To begin, Figure 3 shows the results of DSC measurements heated at a constant rate. The DSC curve for the first measurement run indicates a glass transition in the range 50-60°C.

On the other hand, looking at the portion of the curve above 100°C we see features that may be suggestive of a endothermic peak at 126.7°C and of a thermosetting exothermic peak at 150.8°C—but the data are difficult to interpret.

When faced with ambiguous measurement data of this sort, one strategy for reaching accurate conclusions is *temperature-modulated DSC*, in which the heating profile is periodically modulated by a sinusoidal temperature perturbation. The advantage of temperature-modulated DSC is that, by analyzing the resulting measurement data, effects due to a *reversible* phenomenon such as a glass transition can be separated from effects due to an *irreversible* phenomenon such as enthalpic relaxation or thermosetting exothermic reaction.

A temperature-modulated DSC measurement yields three distinct curves, plotted in Figure 4: (A) the total heat flow, (B) the reversible component of the heat flow, and (C) the irreversible component of the heat flow. Curve (A) simply reproduces the results of the ordinary DSC measurement. On the other hand, inspecting the region near 60°C of curves B (reversible component) and C (irreversible component), we see in curve B a clear signature of a glass transition—allowing accurate determination of the glass-transition temperature—while in curve C we see a endothermic peak due to enthalpic relaxation. Because these two peaks occur at similar temperatures, they cannot be accurately distinguished by ordinary DSC measurements.

Finally, inspecting curve (C) near 150°C, we see that the phenomenon whose interpretation was ambiguous in Figure 3 is now clearly identified as a exothermic peak, and not a endothermic peak—suggesting that previously uncured epoxy resin cure around this temperature.

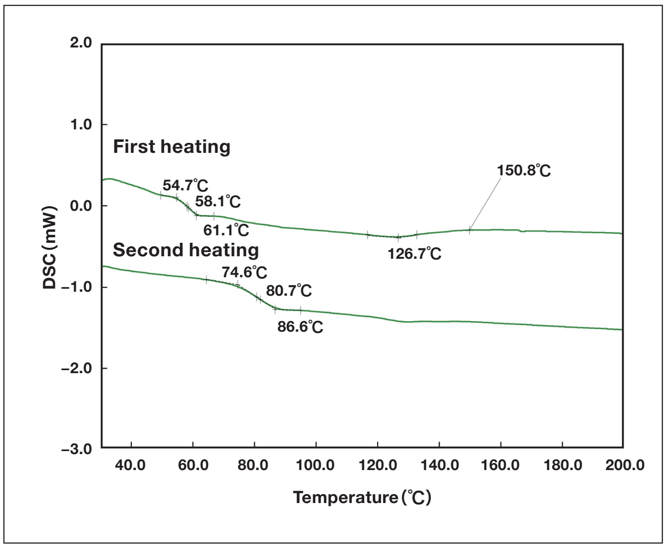

Fig. 3 Ordinary DSC measurement data.

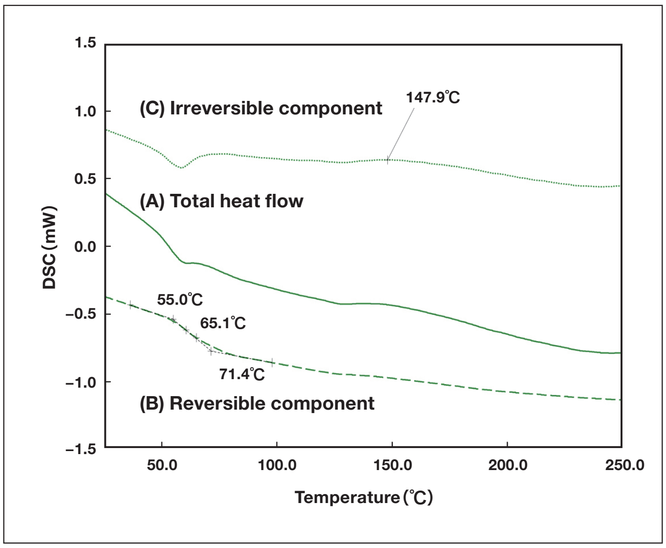

Fig. 4 Temperature-modulated DSC measurement data.

4. Stable Baseline Reproducibility

Instruments in the NEXTA® DSC boast two key structural features: a furnace designed with seamless junction technology extending throughout the entire apparatus—all the way from the heat sink, which constitutes the heater unit, to the cooling-system unit—and heat-insulating walls featuring a 3-layer structure made from low-heat-capacity metals. These structural features allows NEXTA® DSC systems to achieve extraordinarily high baseline stability, with a reproducibility of ±5 µW over the entire measurable temperature range, which extends from −50 to 300°C using an electrical cooling system. This allows accurate evaluation of the thermal properties of even minuscule system components.

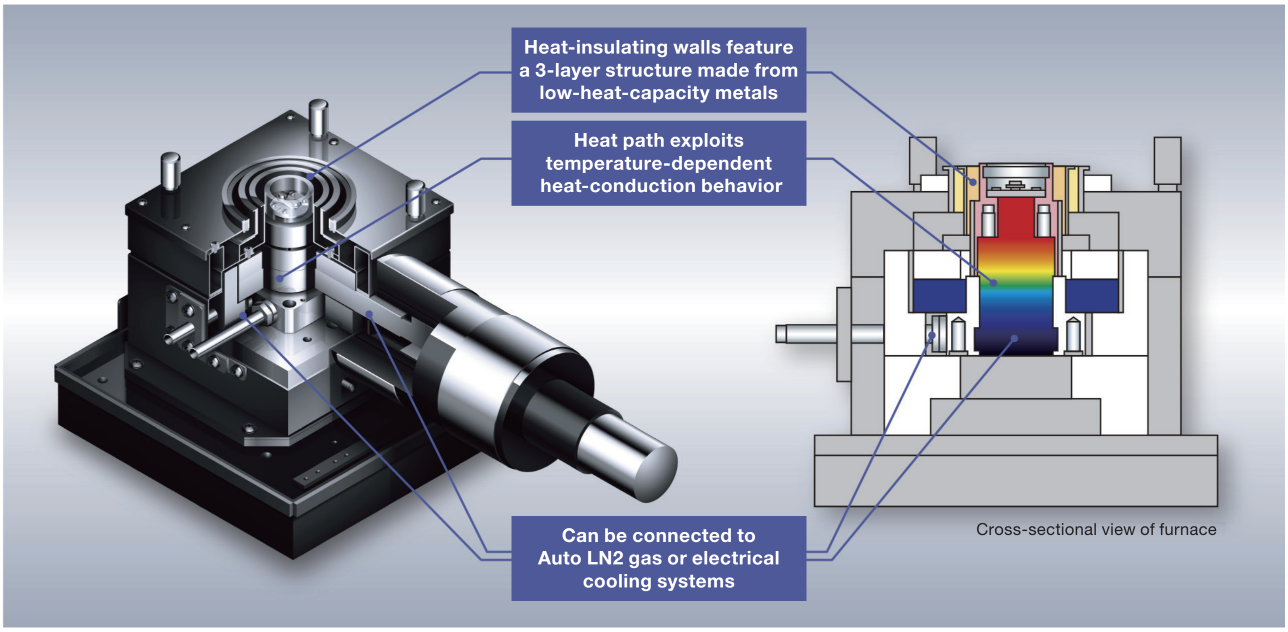

Fig. 5 NEXTA DSC furnace structure.

5. The Real View Unit for Sample Observation at Low Temperatures

The Real View® sample-observation thermal analysis unit enables real-time observation of samples during thermal-analysis measurements, which was not possible with previous-generation systems. Sample-observation images obtained using Real View® are time-synchronized with thermal-analysis data—for example, it is easy to view an image of a sample at the precise moment it passes through a DSC peak.

NEXTA® DSC series instruments are equipped with a high-resolution 2-megapixel camera to enable observation of localized subregions of samples, while their viewports incorporate a heating mechanism to extend the observable temperature range—restricted in conventional instruments to temperatures at or above room temperature—to temperatures as low as −50°C, deep within the low-temperature regime. In addition to allowing samples to be observed at low temperatures, this also opens the door to new methods of *color-space analysis*—quantitative analysis of phenomena that were conventionally characterized by simple visual inspection, including melting points and thermal-insulation behavior accompanying changes in sample color—to address a broader range of measurement needs.

The power of these capabilities is illustrated by an application case study involving real-time observation of an engine-oil sample during low-temperature DSC measurements to determine the cloud point. The *cloud point* of an oil, a threshold temperature below which the fluidity of the oil itself begins to change rapidly, is a key property of great interest in the oil industry—but one which, to date, has often been characterized only by visual inspection.

When engine oil is cooled at a constant rate from room temperature to negative temperatures, a exothermic peak is observed in the vicinity of −15°C. This peak is accompanied by crystallization, a transformation corresponding to the cloud point.

Visual inspection of images indicates that the sample begins to exhibit cloudiness at a temperature near −25°C, an observation corroborated quantitatively by color-space analysis: the brightness L* begins to decrease around this temperature, in conjunction with the exothermic peak. As this example demonstrates, the ability to plot brightness variations in graphical form simplifies the analysis of thermal phenomena and enables measurements at higher precision than can be achieved by visual inspection.

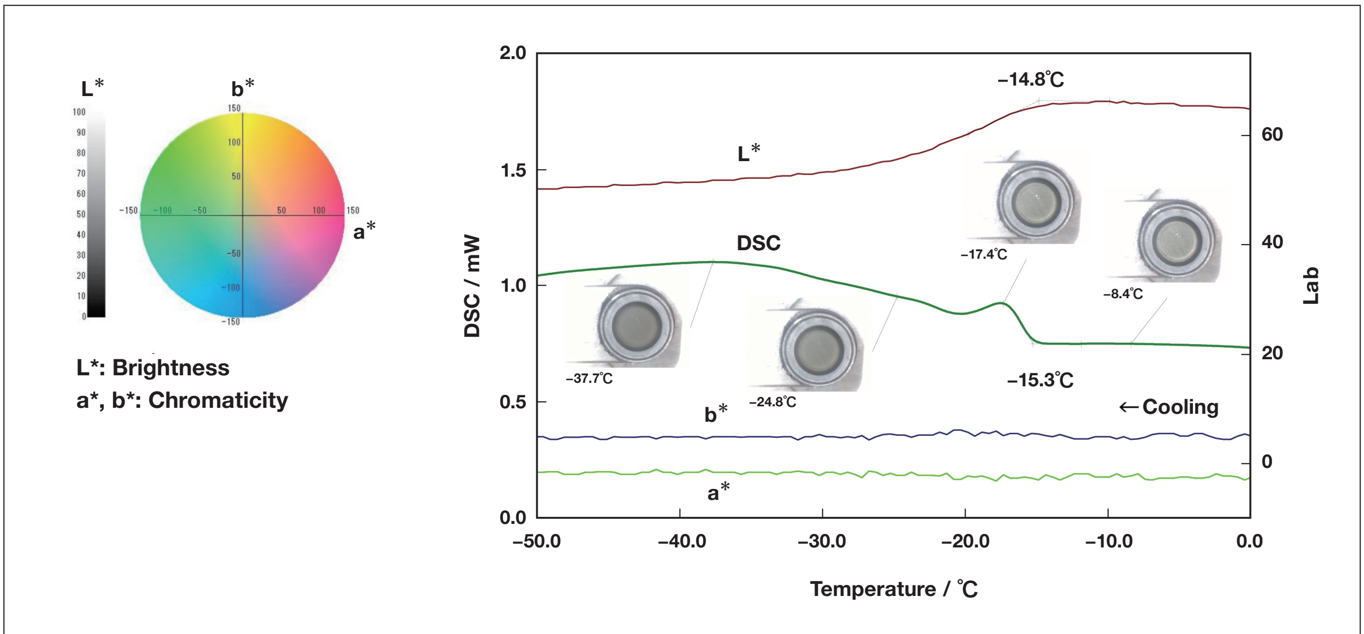

Fig. 6 Cloud-point measurement for an engine-oil sample.

6. Conclusions

The NEXTA® DSC series of thermal analyzers offers high-sensitivity measurements, stable baseline performance, and sample-observation capabilities. These instruments are ideal for high-precision measurements and for analysis or component identification of small-volume samples.

About the author

Shinya Nishimura
Focused Solution Design Department 1
Analytical Instruments Design Development Division
Hitachi High-Tech Science