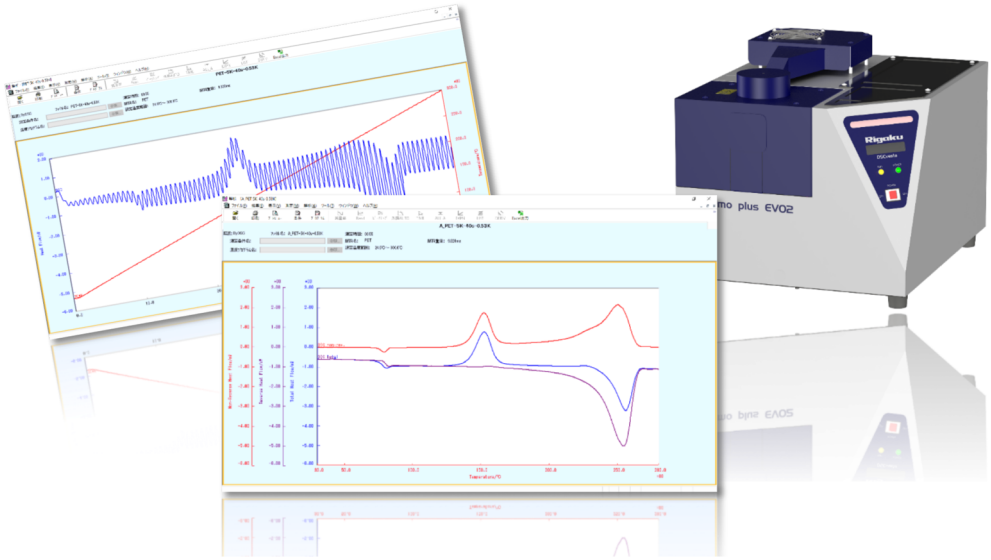
Dynamic DSC Software

—Temperature-Modulated DSC—



1. Introduction

Differential scanning calorimetry (DSC) is a thermal analysis technique that measures the change in heat capacity of a sample, or endothermic/exothermic reactions, based on the difference in temperature between a sample and a reference material that are both heated/cooled at a predetermined constant rate. This technique is widely used to study the thermal information of materials such as glass transition temperature, reaction temperature (e.g. crystallization, melting), and reaction energy. In contrast to conventional DSC, there is a thermal analysis technique called "temperature-modulated DSC," which performs measurements with the addition of temperature-modulating components, such as sine wave and steps, to the constant-rate heating/cooling process (Fig. 1). After the release of ISO (ISO-19935-2) "Plastics-Temperature-modulated DSC" in 2020, this measurement method will likely become widespread. Therefore, Rigaku has developed a control algorithm and the Dynamic DSC Analysis software that uses sine waves as a temperature modulating component.

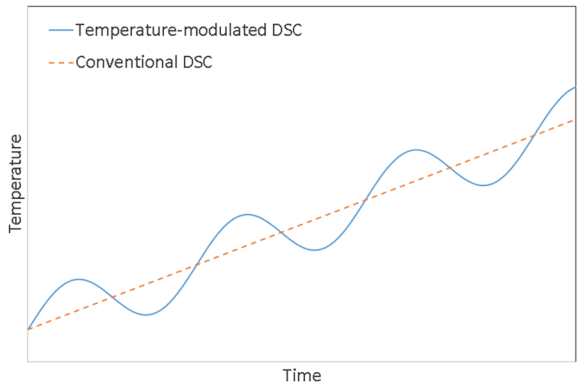


Fig. 1. Comparison of temperature-modulated DSC curve (sine wave) and conventional DSC curve.

2. Dynamic DSC

The measurement data (DSC_{basic}) obtained by the dynamic DSC method is divided into the following three curves through mathematical processing via the Dynamic DSC software (Fig. 2). The first curve is called DSC_{total}, which is a DSC result obtained from the average value during a single wave cycle, and is equivalent to conventional DSC measurement results. The second curve is called Reversing DSC ($DSC_{rev.}$), which is a DSC result calculated from the components following a sine wave. Since the reversing component of the sample follows the sine wave, the result is related to the reversing component of the sample, representing the heat capacity information of the sample. Glass transitions are observed in $DSC_{rev.}$. The third curve is called Non-reversing DSC ($DSC_{non\text{-}rev.}$), which is a DSC result obtained by subtracting $DSC_{rev.}$ from DSC_{total} and does not follow the sine wave, representing a non-reversing component of the sample. Dehydration, crystallization, enthalpy relaxation, etc. are observed in $DSC_{non\text{-}rev.}$.

Figure 2 shows the dynamic DSC analysis result of amorphous polyethylene terephthalate, PET. The

result indicates that the obtained DSC_{total} is similar to the conventional DSC results: a baseline shift with an endothermic peak is observed at 70°C, followed by an exothermic peak and another endothermic peak at 150°C and 250°C, respectively.

In the $DSC_{rev.}$, only the baseline shift due to the glass transition at 70°C and an endothermic peak of melting at 250°C are detected. In the $DSC_{non\text{-}rev.}$, an endothermic peak attributed to enthalpy relaxation and an exothermic peak caused by crystallization are seen at 70°C and 250°C, respectively. Another exothermic peak associated with recrystallization that occurred with a melting can be observed at 200°C.

Thus, dynamic DSC enables the separation of reactions overlapping in the same temperature region, such as glass transition and enthalpy relaxation, which cannot be separated by conventional DSC. This technique has the potential to provide new findings, such as information about recrystallization during melting.

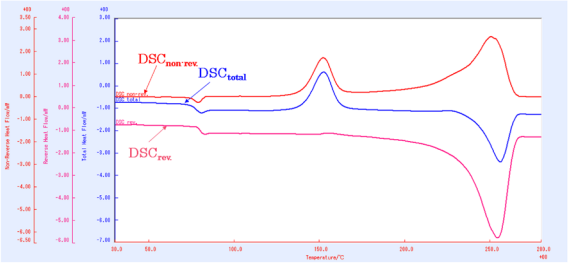


Fig. 2. Dynamic DSC analysis result of polyethylene terephthalate (PET).

3. Main features

3.1. Phase correction function

$DSC_{rev.}$ is calculated as follows: the DSC-modulating component and the temperature-modulated rate component are determined by subtracting their average values per cycle from the obtained DSC_{basic} and obtained temperature change rate, respectively. Then the amplitude of the DSC-modulating component is divided by the amplitude of the temperature-modulated rate component and multiplied by the average temperature change rate per cycle. However, in this calculation, a phase difference occurs between the DSC-modulating component and the temperature-modulated rate component. Since the phase difference is strongly affected by reactions of the sample, it needs to be corrected in order to output an accurate $DSC_{rev.}$ The Dynamic DSC Analysis software allows the correction of phase differences with ease by selecting two unresponsive points on a phase curve that represents a phase difference between the DSC-modulating component and the temperature-modulated rate component.

3.2. Simple specific heat capacity measurement

Measuring the specific heat capacity of a sample by conventional DSC requires the measurement of an empty pan, a reference sample, and a measurement sample. However, using temperature-modulated DSC, only sapphire and a measurement sample are measured. In addition, using a specific heat analysis table creation tool, the specific heat capacity value can be tabulated at any temperature or temperature interval and can be saved in CSV format or printed.

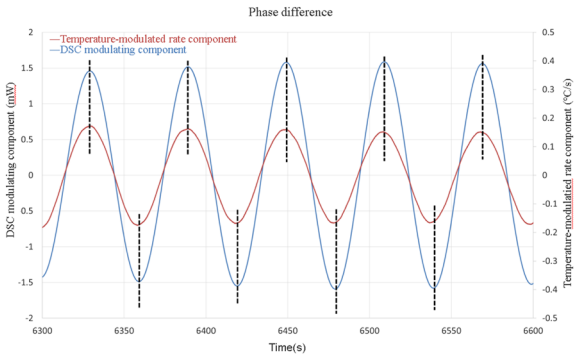


Fig. 3. Phase difference.

3.3. Zero setting of non-reversing DSC

Ideally, in the region where a sample does not undergo a phase transition or chemical reaction, the baselines of DSC_{total} and $DSC_{rev.}$ are equal, and the baseline of $DSC_{non\text{-}rev.}$, which is the difference between DSC_{total} and $DSC_{rev.}$, is 0 mW. In actuality, however, the $DSC_{non\text{-}rev.}$ baseline does not reach 0 mW due to instrument and/or sample pan errors. To solve these errors, the Dynamic DSC Analysis software has a feature that corrects such errors by applying the zero setting to two specified points on the $DSC_{non\text{-}rev.}$, allowing users to directly compare the DSC_{total} and $DSC_{rev.}$ to evaluate the reactions readily.

3.4. Short control cycle

Using Rigaku's small heat capacity furnace and the newly developed control algorithm, a short control cycle of 5 seconds (up to 200 seconds) is achieved without deforming the shape of the sine wave. This improves the accuracy of frequency dispersion analysis.

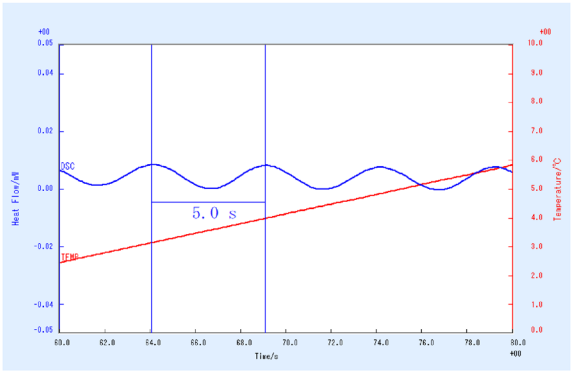


Fig. 4. Dynamic DSC with a cycle of 5 seconds.

3.5. No need for additional devices

Dynamic DSC is available for existing users of ThermoplusEVO2 DSCvesta or DSC8231 by upgrading the firmware and software.

3.6. Plotting different types of separated data

The Dynamic DSC Analysis software is capable of plotting a variety of graphs, such as kinetic DSC ($DSC_{kinetic}$), total specific heat (Cp_{total}), reversible specific heat ($Cp_{rev.}$), and apparent specific heat ($Cp_{app.}$) as well as DSC_{total}, $DSC_{rev.}$, and $DSC_{non\text{-}rev.}$. Also, only the desired graphs can be selected and displayed.

4. Applications

Figure 5 shows the constant heating rate measurement result of terfenadine containing both crystalline and amorphous phases.

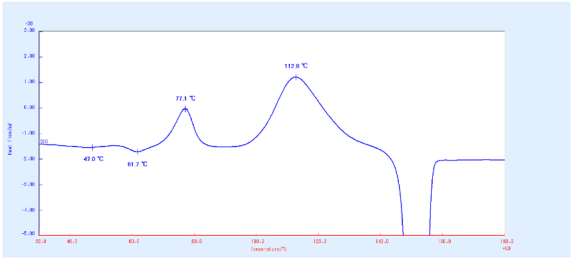


Fig. 5. Constant heating rate measurement result of terfenadine.

Endothermic peaks are observed at 47°C and 62°C, and exothermic peaks are observed at 77°C and 113°C. Since this material contains crystalline and amorphous phases, a baseline shift due to a glass transition is expected, but such changes cannot be observed.

Figure 6 shows the analysis and separation results of the same terfenadine measured by dynamic DSC.

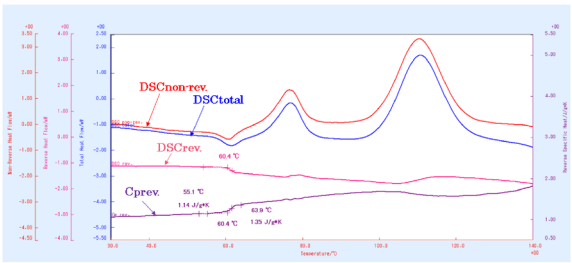


Fig. 6. Analysis results of the terfenadine with dynamic DSC.

The measurement was performed under the conditions of an average heating rate of 3°C/min, a cycle of 36 seconds, and an amplitude of 0.43°C. On the $DSC_{rev.}$, the baseline is slightly shifted in the endothermic direction at 60°C, indicating a glass transition. On the $DSC_{non\text{-}rev.}$, an endothermic peak attributed to enthalpy relaxation is observed at 60°C, and exothermic peaks due to crystallization are observed at 70°C and 110°C. These results reveal that the reversible component (glass transition) and the non-reversing component are separated.

If the specific heat capacity ($Cp_{rev.}$) of the sample is additionally plotted in this graph, it can also be analyzed at any temperatures. Therefore, the dynamic DSC is able to extract the specific heat capacity component, allowing calculation of the specific heat capacity of the sample as well as identification of the presence of a glass transition and its temperature, which may not be identified by constant heating rate measurements.

5. Conclusion

Since dynamic DSC (temperature-modulated DSC) uses a heating/cooling method fundamentally different from that of conventional DSC (constant heating/cooling rate measurement), the obtained information is also different from the conventional, potentially providing new insights into the material. In particular, thermal events related to glass transitions obtained by separating the heat capacity of a sample and the calculation of the specific heat capacity are information that are significant not only for the polymer and pharmaceutical industry but also for other industries.

Since the Dynamic DSC software links all the separated data, it allows even novice users to separate and analyze correct waveforms with ease. Moreover, it also has correction features such as the Zero-setting for $DSC_{non\text{-}rev.}$, to support data interpretation. If you have a DSC module to be upgraded, you can start dynamic DSC measurement without additional hardware. Why not experience dynamic DSC measurement instead of conventional constant heating/cooling rate measurement?