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Application News

No. T156

Thermal Analysis

Physical Properties Evaluation of Polymer Materials by Temperature-Modulated DSC

Differential scanning calorimetry (DSC) is frequently used to evaluate the physical properties of polymer materials, such as the glass transition point, melting point, and thermal decomposition temperature. However, in standard DSC measurements, the peaks and shifts may overlap if multiple thermal phenomena occur in the same temperature range, and analysis of the individual phenomena may be difficult in some cases.

Temperature-modulated DSC (TM-DSC) is a technique that makes it possible to acquire information that cannot be obtained with standard DSC by temperature control in which a modulation is overlaid on a constant temperature increase. In this article, the thermal characteristics of representative polymer materials were evaluated by using the temperature modulation function of the Shimadzu DSC-60 Plus.

A. Kawaguchi

Separation of Heat Flows of Polyethylene Terephthalate

In TM-DSC, temperature control is conducted by overlaying a small-amplitude modulation over a constant temperature increase, as shown in Fig. 1, and as a result, data like those shown in Fig. 2 can be obtained. Data processing of these results using the temperature-modulated DSC analysis program of LabSolutions™ TA makes it possible to obtain the reversing heat flow, which corresponds to changes in specific heat, and the non-reversing heat flow, corresponding to heat absorption and generation, in addition to the total heat flow obtained with the standard DSC. As a typical example in which changes in specific heat and heat absorption and generation occur in the same temperature range, Fig. 3 shows the results of an analysis of a TM-DSC measurement of polyethylene terephthalate (PET). In this measurement, the heating rate was 2 °C/min, the modulation cycle was 40 s, and the modulation amplitude was 0.2 °C.

In the total heat flow (corresponding to the standard DSC curve), the glass transition and enthalpy relaxation overlap at around 75 °C. In the TM-DSC measurements, the baseline shift due to the glass transition appears in the reversing heat flow, while the endothermic peak due to enthalpy relaxation appears in the non-reversing heat flow. Thus, these two phenomena can be separated by the temperature modulation technique.

Furthermore, because the exothermic peak due to crystallization that occurs near 117 °C appears only in the non-reversing heat flow, and an exothermic peak occurs near 231 °C, it can be understood that recrystallization is occurring simultaneously with melting.

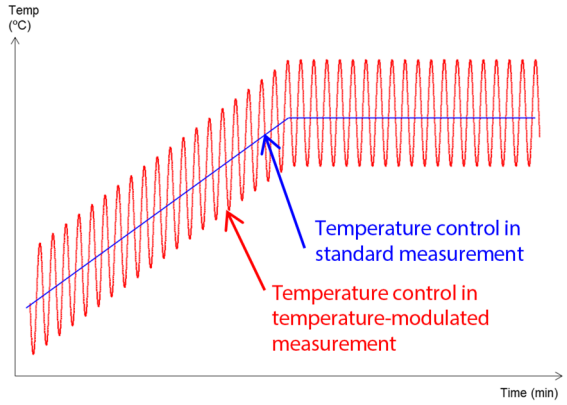

Fig. 1 Temperature Control in TM-DSC

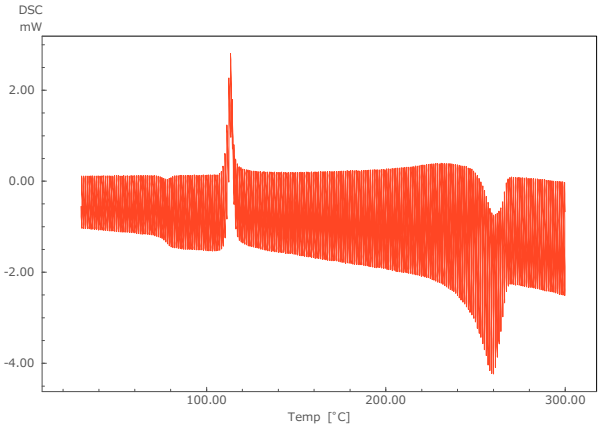

Fig. 2 TM-DSC Curve of PET

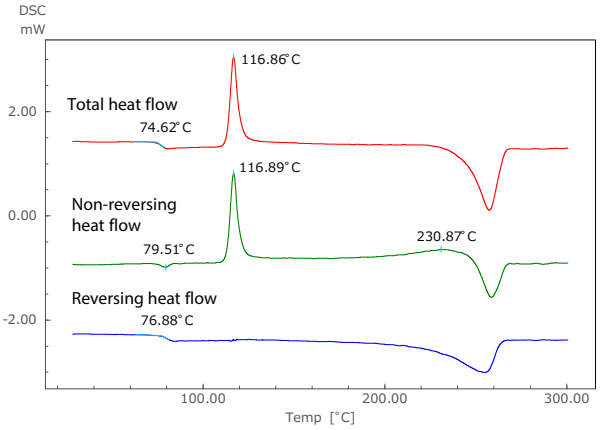

Fig. 3 Analysis Results of TM-DSC Measurement of PET

Melting Behavior of Nylon 6

A TM-DSC measurement of nylon 6, which was heat-treated at a cooling rate of -30 °C/min after melting, was conducted at a heating rate of 2 °C/min, modulation cycle of 80 s, and modulation amplitude of 0.5 °C. Fig. 4 shows the analysis results. Although nylon 6 is a crystalline polymer, owing to its thermodynamically metastable state, overlap of the exothermic peak (at around 193 °C) due to recrystallization appears before the endothermic peak due to melting when it is heated at a slow heating rate. The endothermic peak due to melting near 222 °C in the total heat flow appears in the reversing heat flow, while the exothermic peak due to crystallization appears in the non-reversing heat flow. The exothermic peak overlapping the endothermic peak can be separated by TM-DSC measurement.

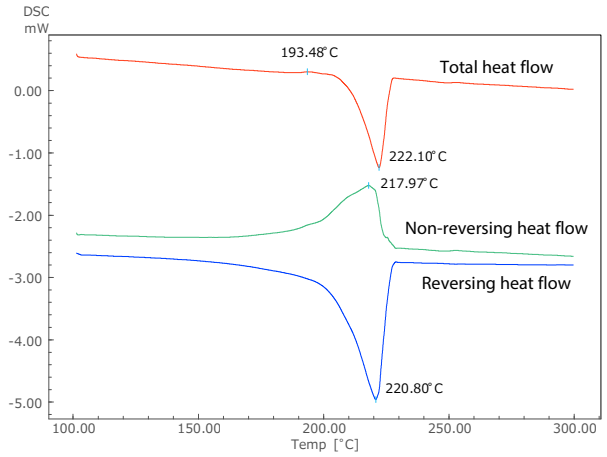

Fig. 4 Analysis Result of TM-DSC Measurement of Nylon 6

Measurement of Epoxy Resin Adhesive

TM-DSC measurements were carried out with epoxy resin-based adhesives that harden as a function of time when two components are mixed. Fig. 5 and Fig. 6 show the measurement results for two samples when the curing time at room temperature was changed to 4.5 h and 42 h, respectively. The measurements were conducted at a heating rate of 3.5 °C/min, modulation cycle of 60 s, and modulation amplitude of 0.5 °C. Looking at the total heat flow, the glass transition occurs near -19 °C in Fig. 5, which shows the short (4.5 h) curing time, but at around 32 °C in Fig. 6, showing the long (42 h) curing time. Moreover, the size of the exothermic peak due to curing also becomes smaller from Fig. 5 to Fig. 6. Thus, it is possible to measure the shift of the glass transition to a higher temperature as curing progresses, and the condition of the decrease in heat generation due to curing by DSC (total heat flow).

On the other hand, as can be seen in Fig. 6, the glass transition and the exothermic peak due to hardening are difficult to identify in the total heat flow, as they occur in close proximity.

However, the two can be clearly identified in the non-reversing and reversing heat flows, as the exothermic peak due to curing is separated to the non-reversing curve, and the baseline shift associated with the glass transition is separated to the reversing curve. Focusing on the glass transition, although the endothermic peak due to enthalpy relaxation and the baseline shift due to the glass transition overlapped in the total heat flow in both Fig. 5 and Fig. 6, they are separated in the non-reversing data and reversing data. In particular, in Fig. 5, enthalpy relaxation may have been overlooked in the standard DSC (total heat flow) owing to its slight change.

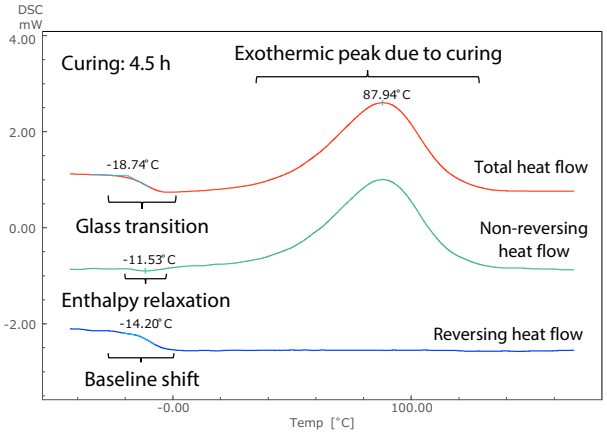

Fig. 5 Analysis Results of TM-DSC Measurement of Epoxy Resin-Based Adhesive (Curing: 4.5 h)

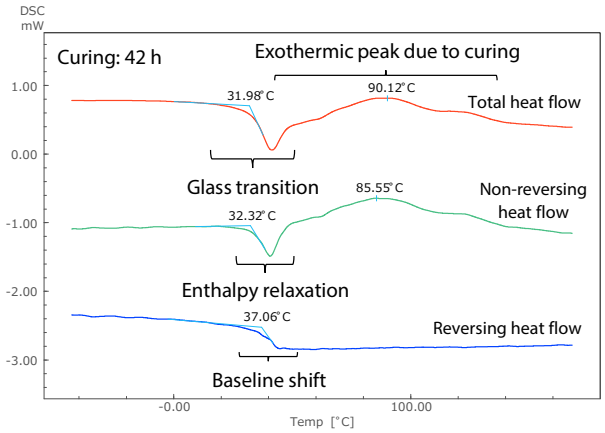

Fig. 6 Analysis Results of TM-DSC Measurement of Epoxy Resin-Based Adhesive (Curing: 42 h)

As introduced here, when examining complex changes in sample data, for example, when reactions and transitions occur simultaneously, temperature-modulated DSC makes it possible to acquire knowledge and information that cannot be obtained with standard DSC alone.

First Edition: Mar. 2020

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