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NEW APPLICATIONS OF THE AUTOMATIC THERMAL ANALYSIS SYSTEM *

JIM PENN and NOBUO MASTUMORI

Seiko Instruments U.S.A., Inc., Scientific Instruments Division, Torrance, CA (U.S.A.)

RYOICHI KINOSHITA and YOSHIKO TERAMOTO

Seiko Instruments, Inc., Scientific Instruments Division, Tokyo (Japan)

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ABSTRACT

The Automatic Thermal Analysis System has been developed because of the recent demand for improved efficiency of thermal analysis. The system is able to automate heating and cooling measurements for differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and TMA/SS (stress, strain control TMA) over a wide temperature range. A program-controlled liquid nitrogen gas cooling system is used with the same capabilities (reproducibility, noise level, etc.) for cooling and heating measurements.

As a result of this automation, not only has the efficiency of thermal analysis work improved, but the following new applications have been made possible: (1) specific heat capacity measurement for DSC in cooling mode; and (2) characterization of plastic samples during cycle heating and cooling for TMA and DSC.

INTRODUCTION

Automation and labor saving functions have recently been requested by many users of thermal analysis instruments, as a means of improving the efficiency of thermal analysis work. Thermal analysis (TA) instruments of better capability are also required. The Automatic Thermal Analysis System SSC 5200 Series has been developed to respond to these needs.

The new automatic differential scanning calorimetry (DSC), thermomechanical analysis (TMA) and TMA/SS (stress, strain control TMA) functions give good reproducibility for both heating and cooling measurements, with the automatic cooling system. Some new applications with this system are introduced.

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Figure 1 shows the configuration of the new SSC 5200 Series Automatic TA System. The series consists of a group of analysis modules, a TA disk station and an output device. The analysis modules include six types of DSC, two types of TG/DTA, three types of TMA and two types of TMA/SS module. A total of 13 types of module are available.

The SSC 5200 System is a multi-task system which can have three modules (of the same type or different types) connected to the TA disk station. This system can control the modules simultaneously, and can analyze and output the data from them.

The TA disk station has a 32-bit CPU, a RAM file that can save 80,000 sets of data, a 20 or 40 MB hard disk, and a built-in 3.5 in floppy disk drive. The operator uses a keyboard to carry out data storage, searching and analysis using an OS (operating system). Application software designed especially for thermal analysis can also be accessed, while monitoring the procedures on a color CRT.

The analysis modules with a "C" suffix—the DSC 220C, TMA 120C and TMA/SS 120C modules—can be attached to an automatic liquid N_2 gas cooling system, enabling fully automatic heating and cooling measurements throughout the entire measurement range. These modules have two control loops. The first is for precise temperature control of the furnace heater by

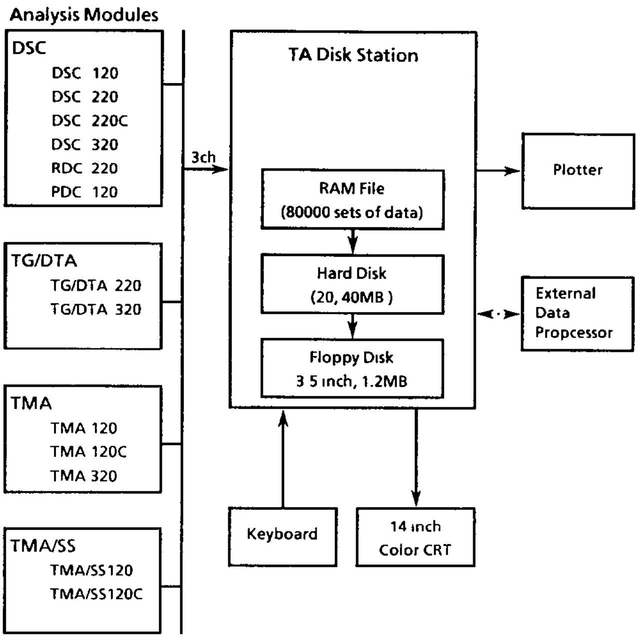

Fig. 1. SSC 5200 TA system configuration.

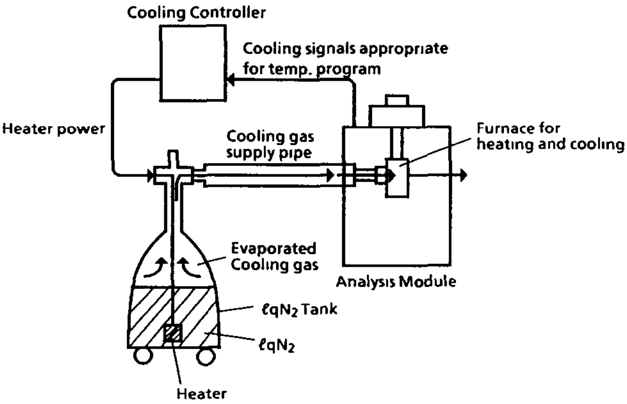

Fig. 2. Automatic gas cooling system operating principle.

the temperature program. The second controls the cooling gas flow to the furnace area.

The principle of the automatic gas cooling system is explained in Fig. 2. When the temperature program is running, the module sends appropriate cooling control signals to the cooling controller, as well as regulating the temperature of the heater in the furnace. The cooling controller then supplies the heater inside the liquid nitrogen tank with the appropriate amount of power. This heater evaporates some of the liquid nitrogen, producing cooling gas, which flows through the gas supply pipe, cools the furnace area, and is then released into the air. In this manner, the furnace functions both to heat and cool the sample automatically, according to the temperature program.

APPLICATIONS

This automation of heating and cooling measurement has made it easy to make highly reproducible cooling measurements at low temperatures, a task that was quite difficult in the past. Several new applications have resulted from this.

DSC measurement of specific heat capacity during the cooling process

Figure 3 shows the heating and cooling DSC curve for the measurement of the specific heat capacity of a polystyrene sample near its glass transition temperature. This analysis was performed at a heating/cooling rate of 10 °C min^{-1}, utilizing sapphire as a standard reference material. Since a highly reproducible baseline is obtained even during the cooling process, it is easy to make highly reproducible specific heat capacity measurements.

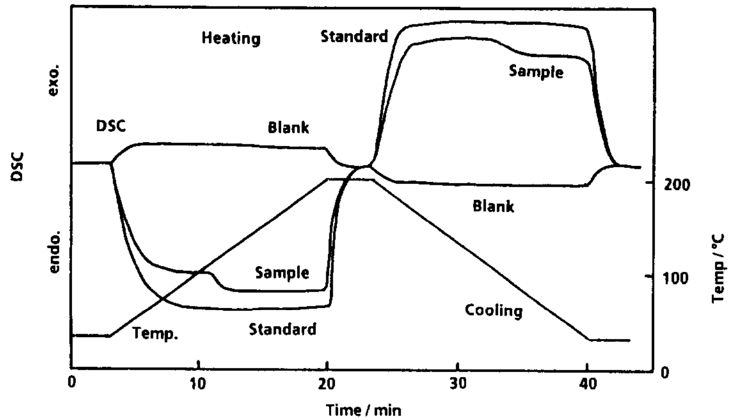

Fig. 3. DSC curves for measurement of specific heat capacity.

Figure 4 is a plot of the specific heat capacity of polystyrene heated and cooled at 10 °C min^{-1}. The specific heat capacity values before and after the glass transition match for both heating and cooling measurements, but they differ near the glass transition temperature, showing that hysteresis is present. The specific heat capacity of liquid samples in super-cooled states can only be calculated from cooling measurements.

Figure 5 is a plot of the specific heat capacities of H_2O and D_2O (heavy water) calculated from cooling measurements. The measurement conditions were to start from a temperature of 80 °C and cool at a rate of 5 °C min^{-1} down to an end-point temperature of −50 °C. However, the data are displayed only to the point at which the change occurs from the super-cooled state to ice. The specific heat capacity values increase as the temperature

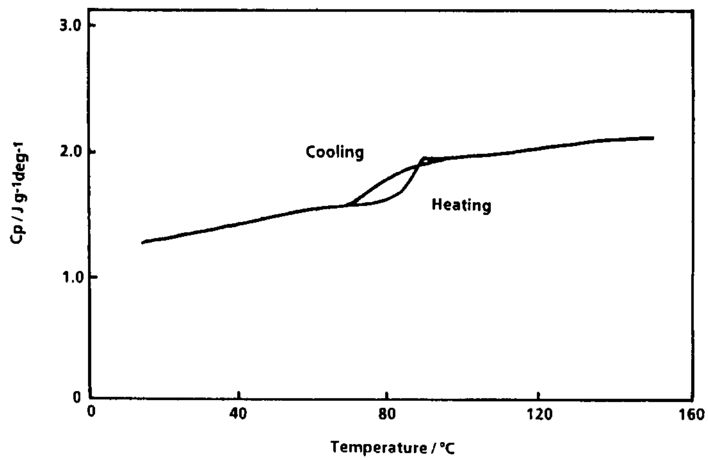

Fig. 4. Specific heat capacity of PS sheets.

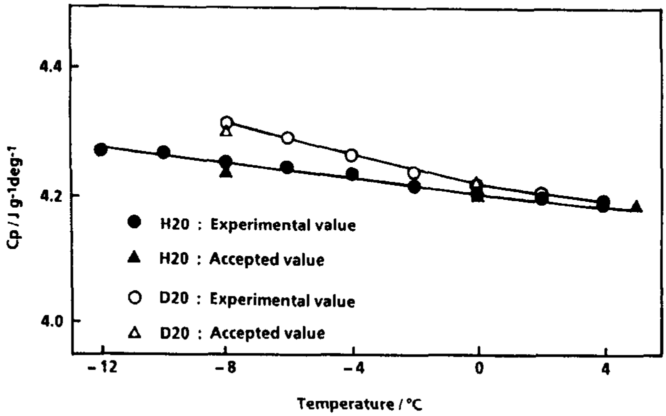

Fig. 5. Specific heat capacity of H_2O and D_2O.

drops, and the difference between H_2O and D_2O can be clearly seen. The values also agree well with accepted values (marked with a triangle) [1–3].

Figure 6 is a plot of the specific heat capacity of glycerol and has glass transition around $-90\,°C$, calculated from cooling and heating measurements. Cooling and heating were both at $10\,°C\ min^{-1}$. The shift of specific heat capacity owing to the glass transition is observed around $-90\,°C$, with different values for cooling and heating.

Above and below the glass transition temperature, the specific heat capacity values match for the heating and cooling processes. This shows good performance of the DSC 220C for sub-ambient cooling and heating measurement.

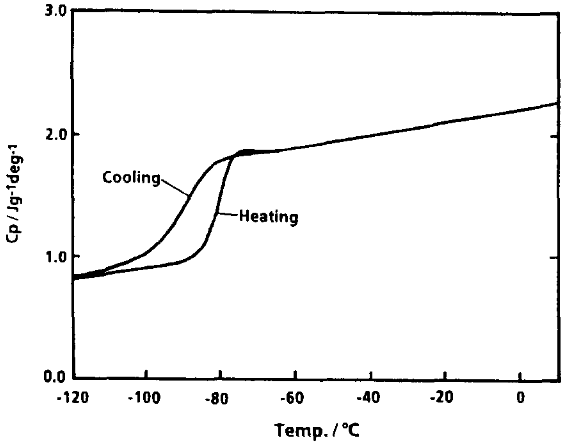

Fig. 6. Specific heat capacity of a glycerol sample.

Heating and cooling measurements for TMA and DSC

Figure 7 shows TMA data for a chloroprene rubber sample cooled and heated at 5 °C min^{-1} in the temperature range from room temperature to −100 °C. The glass transition can be seen as an abrupt change of slope in the TMA curve near −53 °C for both heating and cooling. The glass transition values for heating and cooling calculated from the TMA curve are both −53 °C, showing that the results agree.

The linear expansion coefficients of the sample for heating and cooling calculated from the TMA curve slope at the lower and upper glass transition temperatures are also in good agreement.

Figure 8 shows the TMA curve for a thermoset polymer sample which was repeatedly heated and cooled at 5 °C min^{-1}. The TMA curve for the first heating shows the sample expansion stopping temporarily near the glass transition temperature and then continuing after that. In the cooling data after the first heating, and in the second heating data this does not occur, the only simple changes of the TMA curve slope being those associated with the glass transition.

It appears that the change in the TMA curve in the first heating is associated with the release of strain, and that after the temperature has been raised once, the strain is gone.

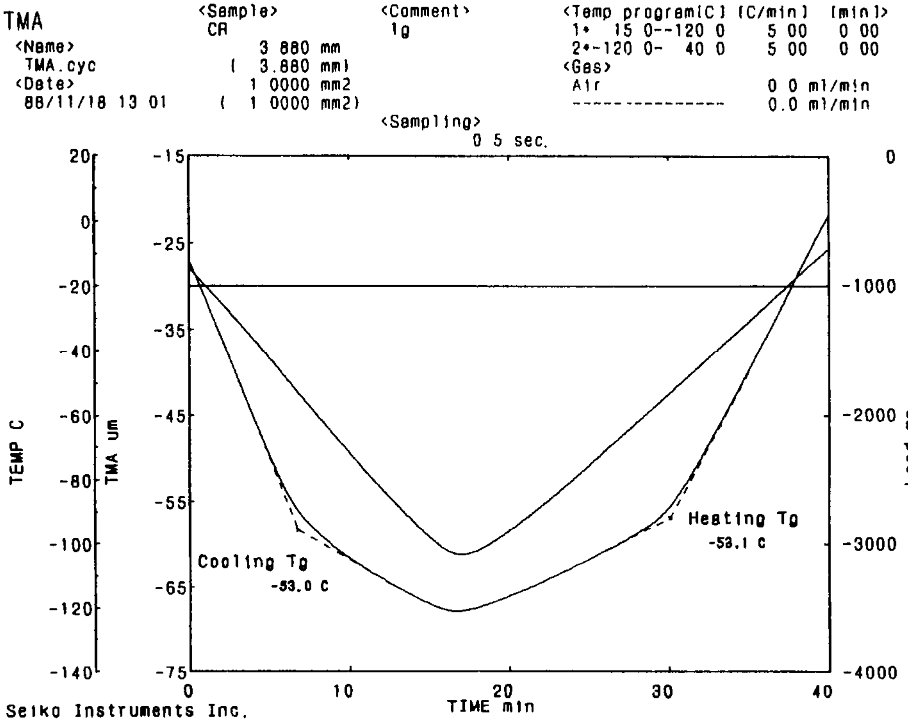

Fig. 7. TMA heating and cooling data for a chloroprene rubber sample.

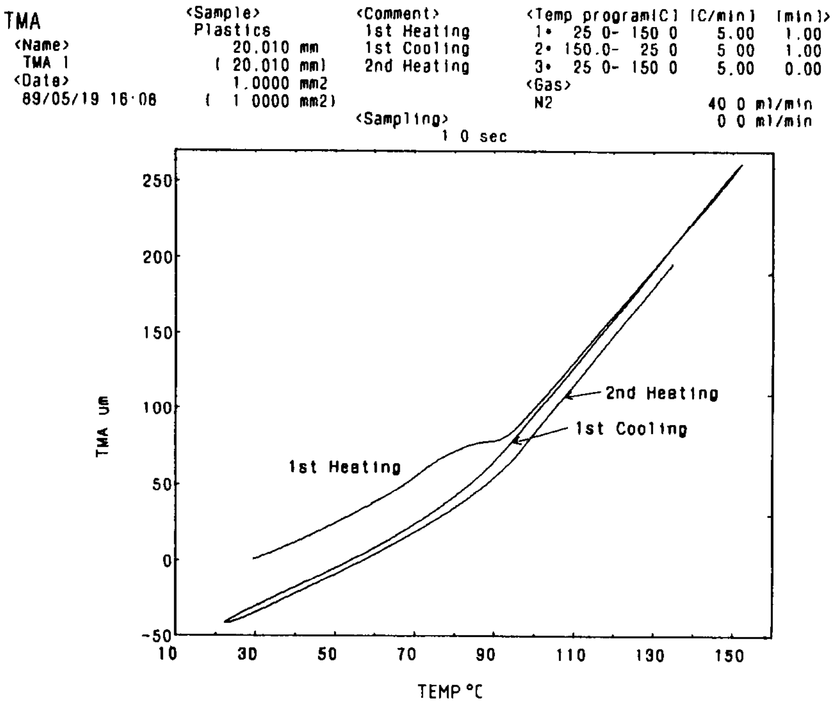

Fig. 8. Cyclic TMA data for a thermoset polymer sample.

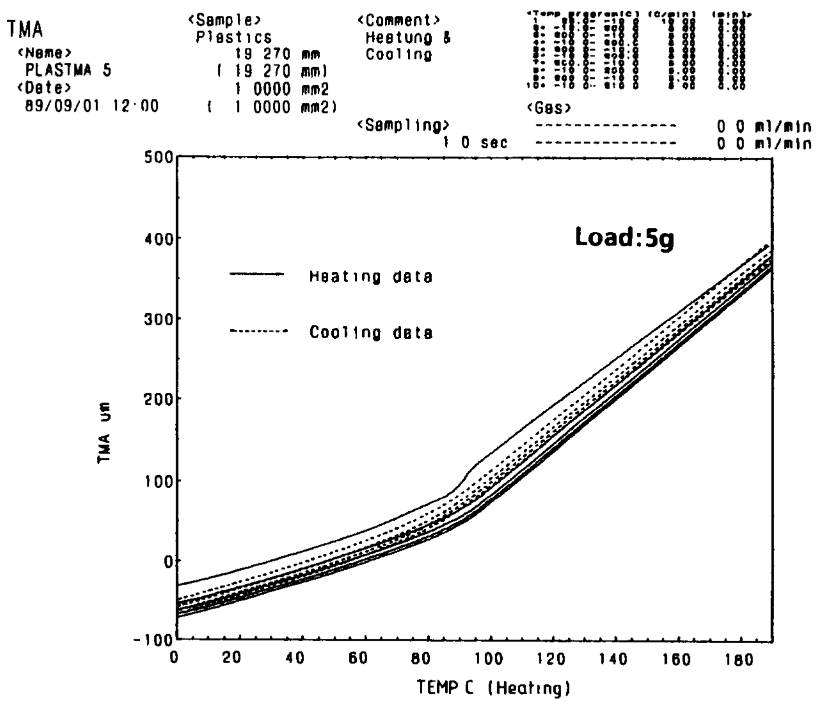

Fig. 9. Cyclic TMA data for a sample of plastic.

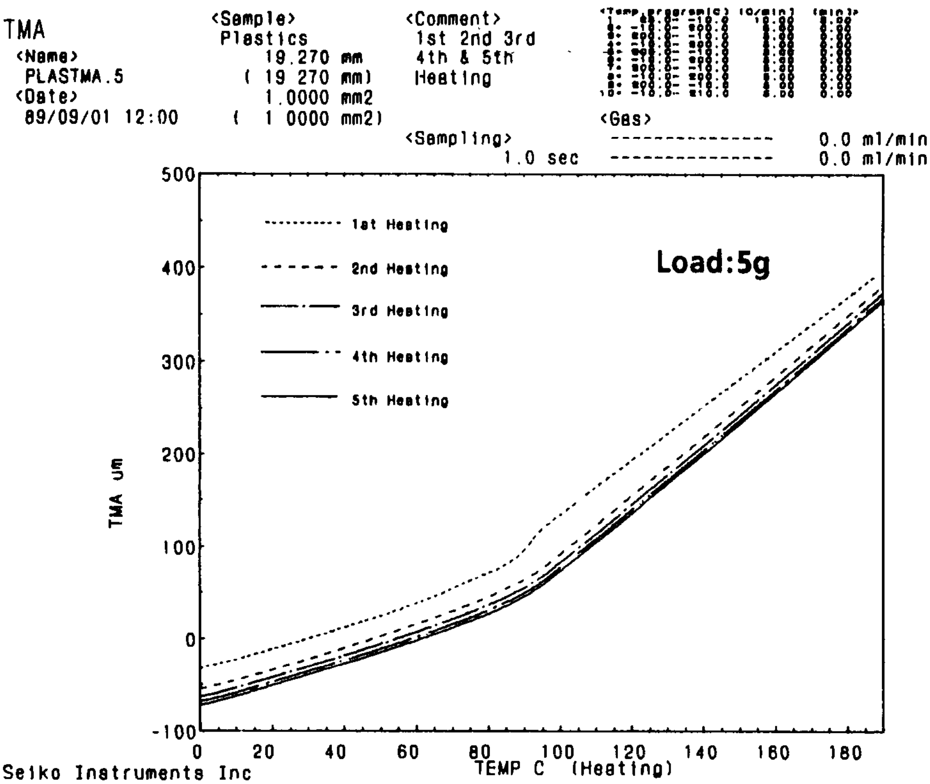

Fig. 10. Cyclic TMA data for a sample of plastic (heating only).

Figure 9 also shows the TMA curve for a sample of plastic which was heated and cooled for five cycles at 5 °C min^{-1}. The load on the sample was 5 g. The continuous lines are heating measurements and the dotted lines are cooling measurements.

Figure 10 shows the plot of heating curves from Fig. 9. The first heating curve (small dotted line) has anomalous expansion around 90 °C. This phenomenon does not appear in other heating curves (second, third, fourth and fifth), which show only a simple change of expansion owing to the glass transition of the sample. After the first heating, it is observed that the sample length becomes shorter than the initial length. The shrinkage amount is decreased by the number of the cycle.

Figures 11 and 12 show the DSC curve for the same sample of plastic heated and cooled repeatedly at 5 °C min^{-1}. As can be seen, the glass transition temperature in the first heating curve is lower than that in other heating curves. After the first heating, good reproducibility is observed in the DSC curve, and the glass transition temperatures in each of the heating and cooling DSC curves are very similar.

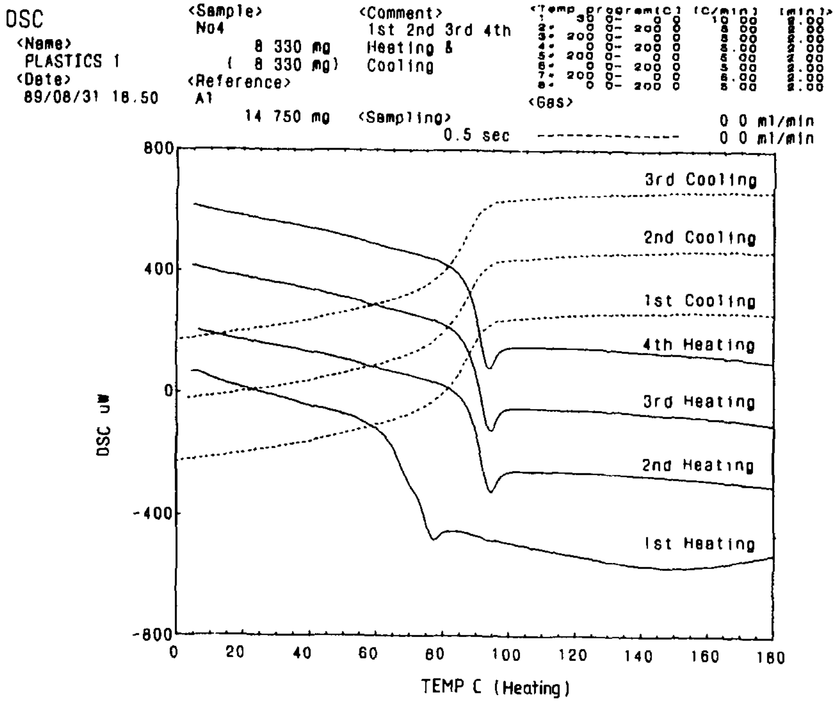

Fig. 11. Cyclic DSC data for a sample of plastic.

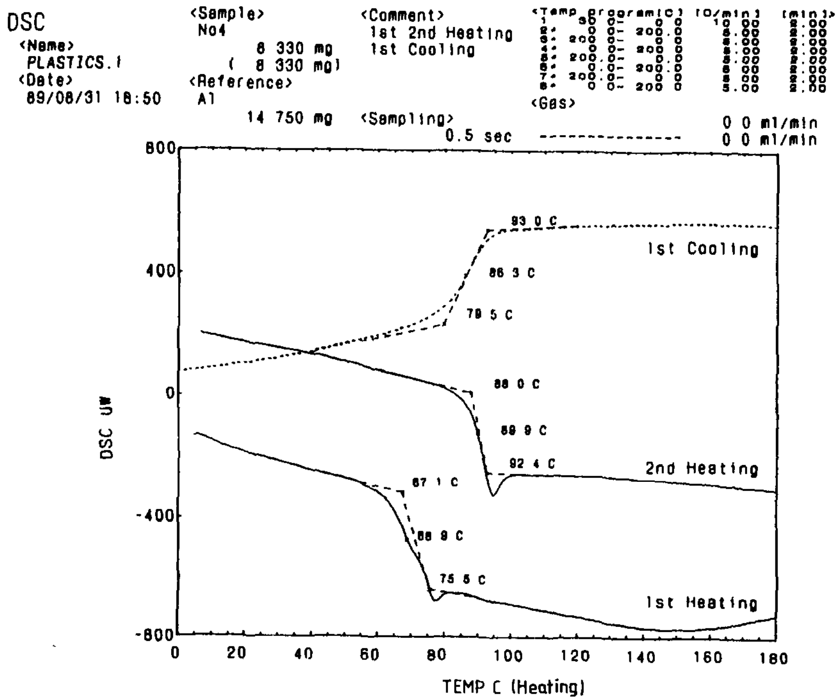

Fig. 12. Glass transition plot of DSC heating and cooling data for a sample of plastic.

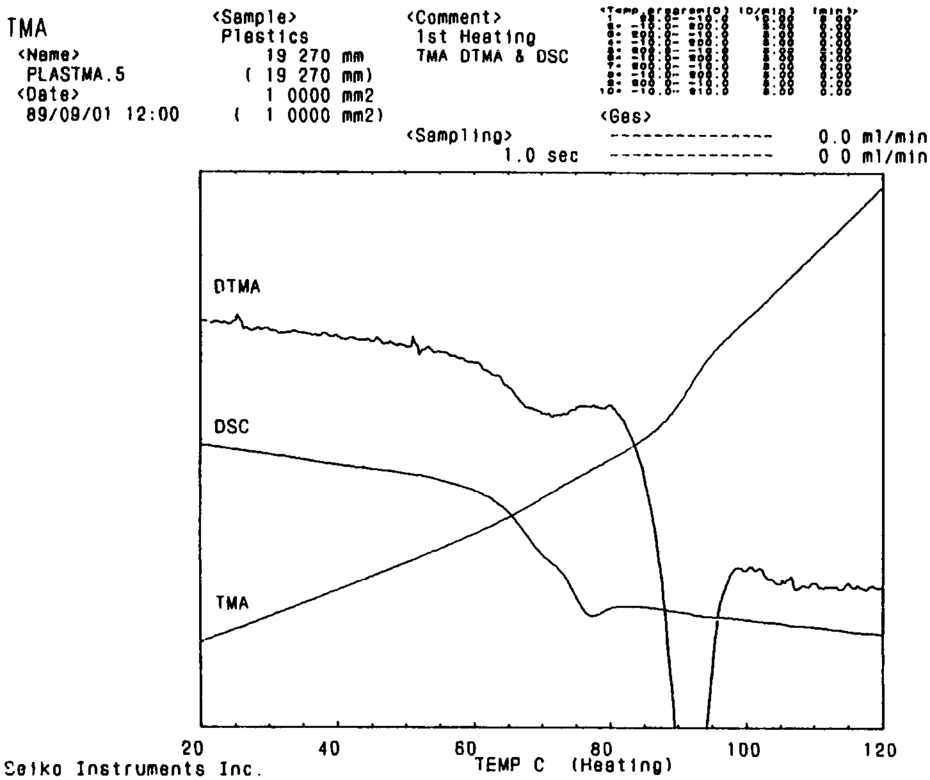

Fig. 13. Comparison of TMA, DTMA and DSC curves for a sample of plastic (first heating).

Figure 13 shows a comparison plot of the TMA, DTMA and DSC curves for the first heating of the sample of plastic. When the baseline of DSC starts to shift owing to the glass transition, the same type of change is observed in the DTMA curve. This means the expansion rate starts to change at the beginning of the glass transition.

On the other hand, the anomalous expansion which is observed in the first TMA curve occurs after the glass transition is finished in the DSC curve. This means the relaxation of the strain in this sample occurs concurrently with the rapid expansion after the glass transition.

CONCLUSION

The new SSC 5200 Series Automatic TA System provides automated heating and cooling measurements with good reproducibility. The system makes it easy to examine thermal histories using TMA heating and cooling measurements, and to perform DSC cooling measurements of specific heat capacity, which have previously been difficult to evaluate. There are many possibilities for wider application of this system in the future.

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