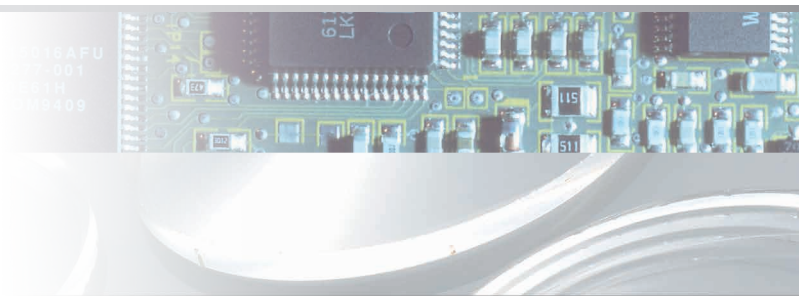
C160-E010B

SHIMADZU
Excellence in Science

Thermal Analysis 60 Series

Application Data Book

Polymer and Electronic Material



Contents

1 Plastic

1.1 Influence of heat treatment on polyethyleneterephthalate (PET)

■Explanation

PET bottle was measured by DSC. With the original sample, the peak by melting is mainly observed at 254.8 ˚C. It shows that the structure before heating was crystalline. On the other hand, as for DSC (2nd-heating) of an original sample which is cooled rapidly after heating, glass transition is observed at 77.6 ˚C. Because the glass transition occurs in a non-crystalline solid, it turns out that the PET becomes non-crystalline when it is cooled rapidly. The exothermic peak at 136.8˚C means that the non-crystalline PET changes to the crystalline PET at this temperature.

■Analytical Conditions

Instrument	: DSC-60
Sample	: PET
Sample Amount	: 6.72mg
Atmospheric Gas	: N_2
Flow Rate	: 50mL/min
[Temperature Program]	
Heating Rate	: 10˚C/min

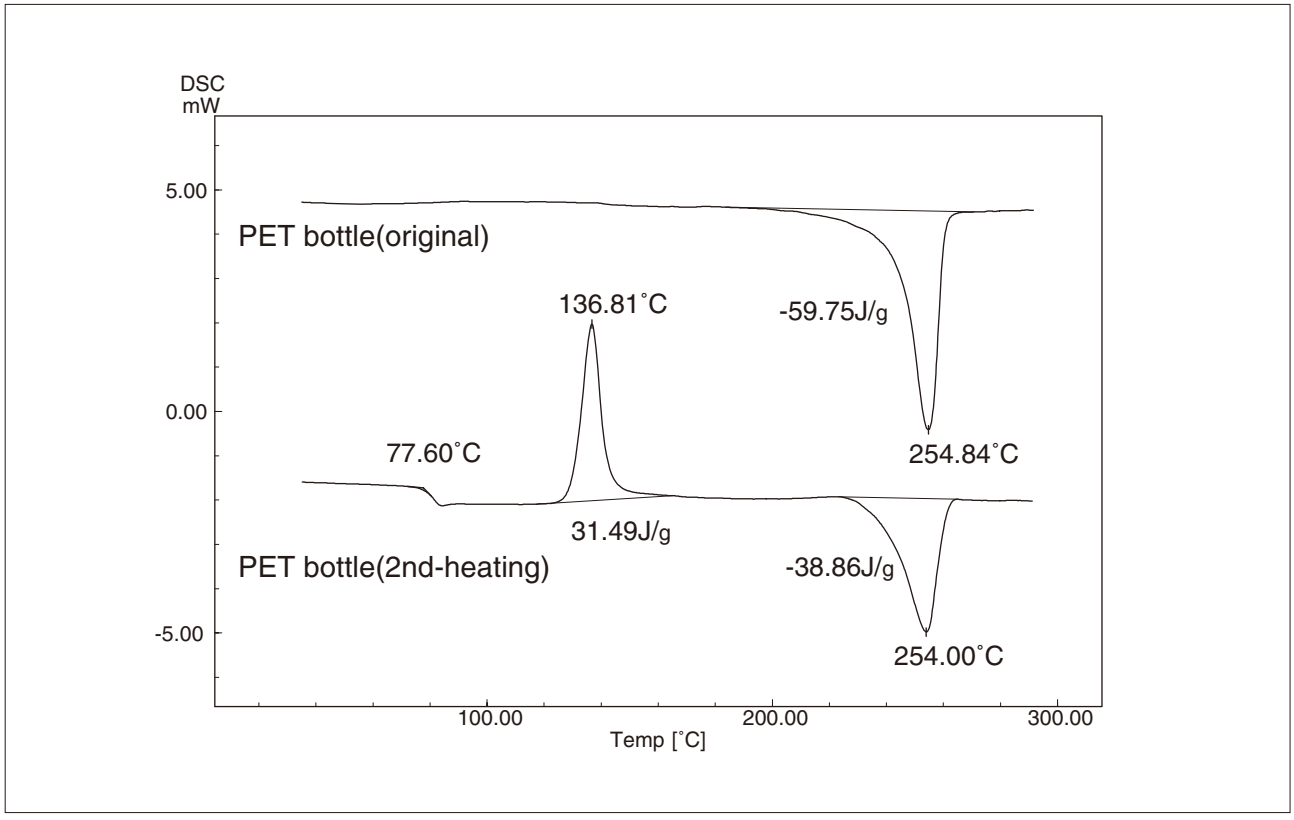


Fig. 1.1.1 DSC curves of PET bottle (original and 2nd-heating)

1.2. Heat history of polyetheretherketone (PEEK)

■Explanation

It is known that the thermal character and the mechanical property which polymer material has will change a lot with the heat history which material received. In the case of a thermoplastic resin, since solid crystal structure changes depending on the cooling speed after melting, if the sample which the cooling speed differ is heated by DSC, many case where a difference is observed in peak form will be seen. Since glass transition is observed at 144.6˚C, film-like PEEK is non-crystalline. On the other hand, since only the melting at 339.2˚C is mainly observed, the block form PEEK is crystalline. In spite of being same PEEK, it is expected that the film does not crystallize since it was cooled rapidly in molding, and that the block was cooled gradually and crystallized well.

■Analytical Conditions

Instrument	: DSC-60
Sample	: PEEK film
Sample Amount	: 5.86mg
Sample	: PEEK block
Sample Amount	: 8.44mg
Atmospheric Gas	: N_2
Flow Rate	: 50mL/min
[Temperature Program]	
Heating Rate	: 20˚C/min

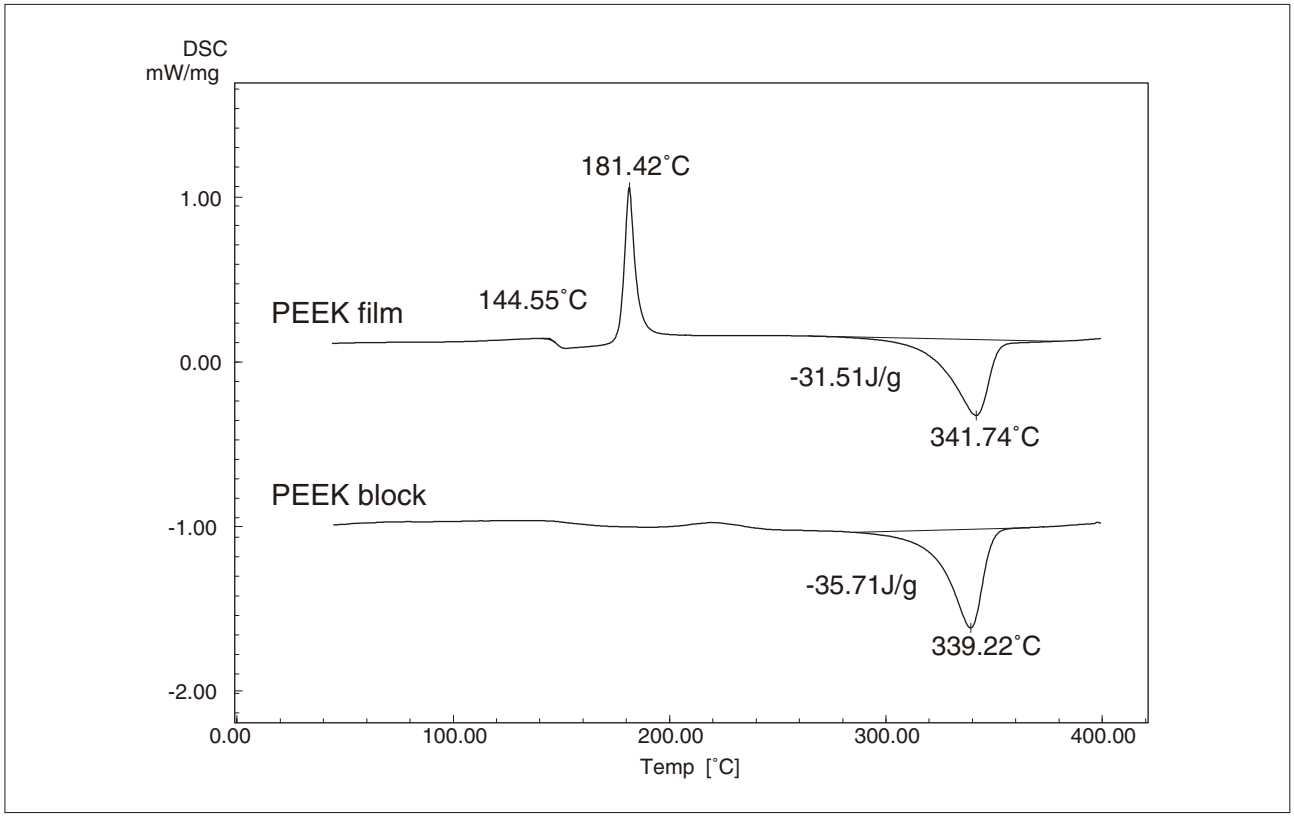


Fig. 1.2.1 DSC curves of PEEK

2 Characterization by Melting and Crystallization

2.1 Melting and crystallization of nylon A and B

■Explanation

The melting and the crystallization of nylon A and B which a lot differs were measured.
In melting process, a difference is looked at endothermic peak width by the difference in a lot. The exothermic peak form by crystallization differs in cooling process, and the difference between lots is seen further notably.

■Analytical Conditions

Instrument	: DSC-60
Sample	: nylon A
Sample Amount	: 5.35mg
Sample	: nylon B
Sample Amount	: 5.52mg
Atmospheric Gas	: N_2
Flow Rate	: 40mL/min
[Temperature Program]	
Heating Rate	: 10˚C/min
Cooling Rate	: -10˚C/min

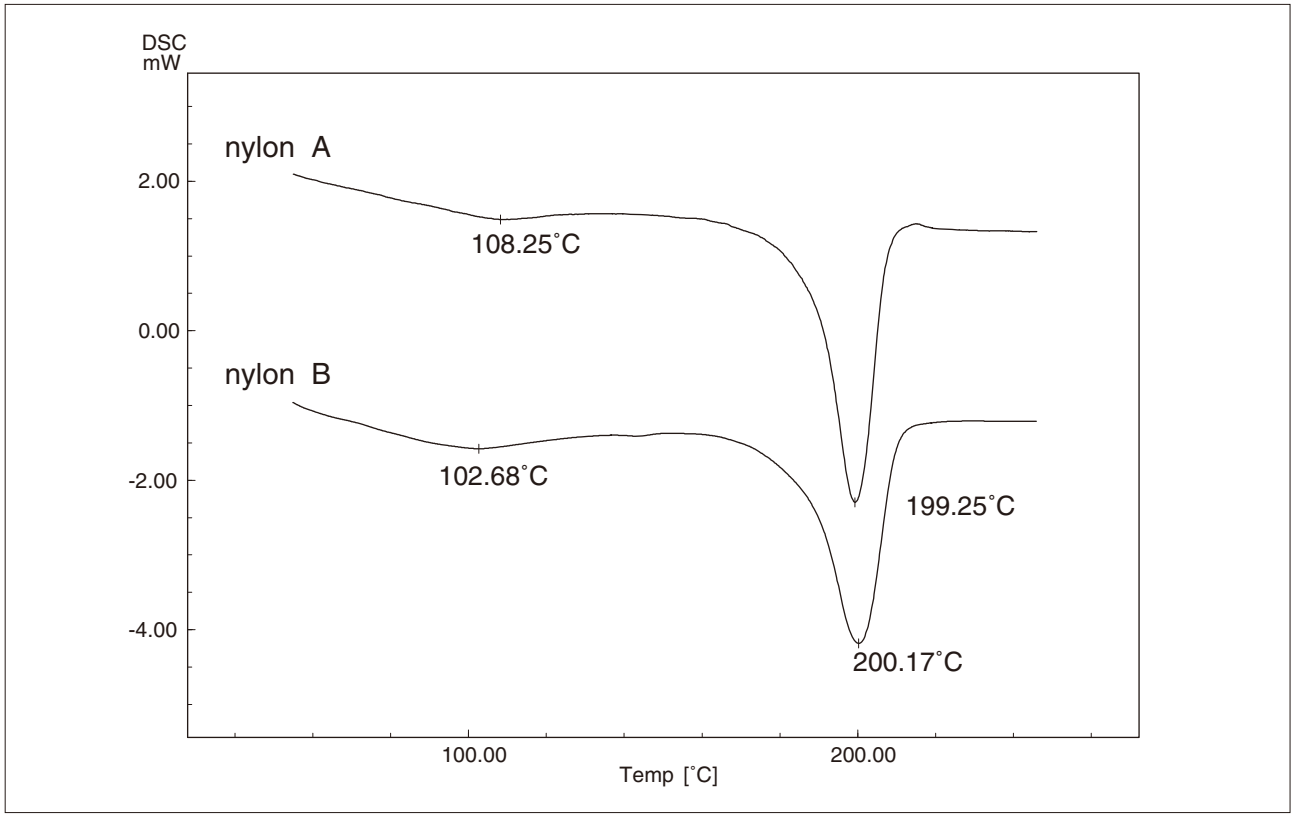


Fig. 2.1.1 DSC curves of nylon A, B (melting)

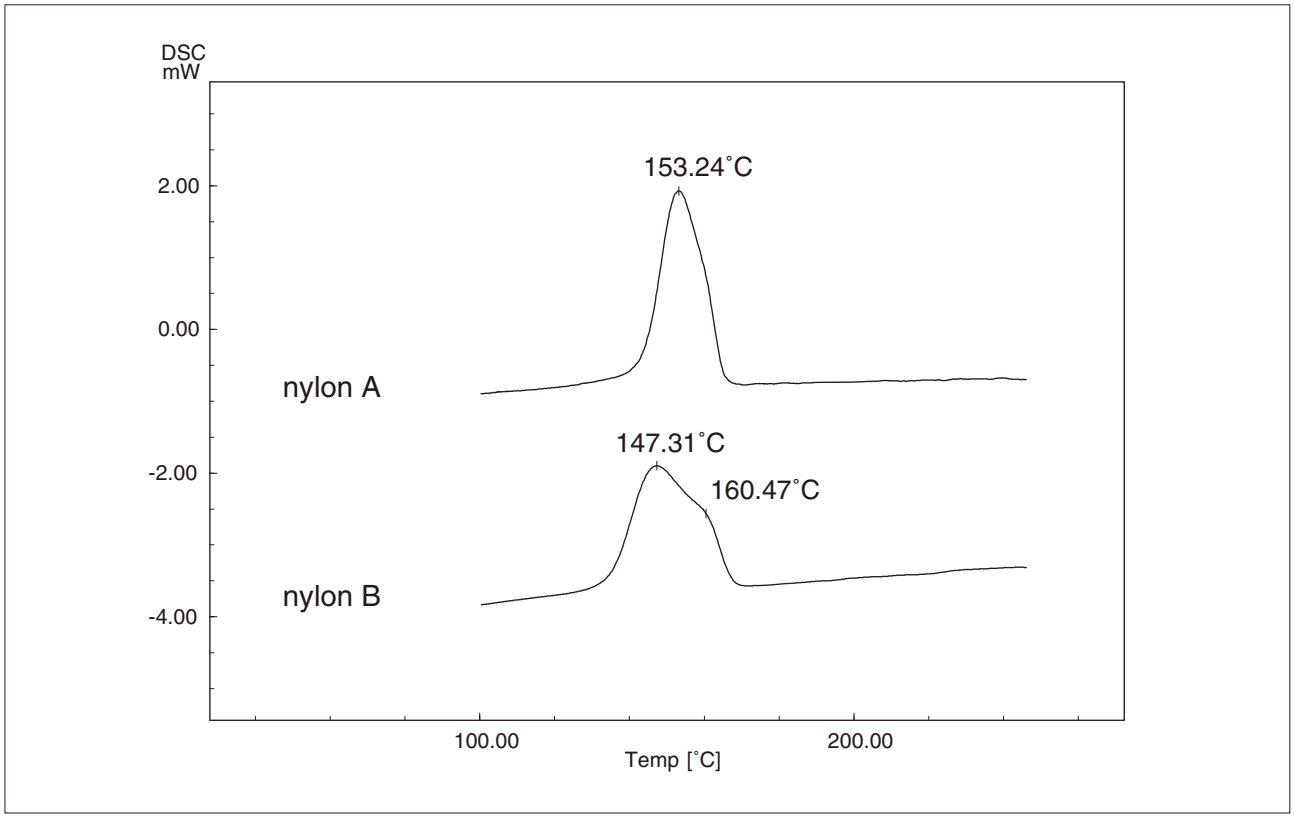


Fig. 2.1.2 DSC curves of nylon A, B (crystallization)

2.2 Analysis of original and the heat treatment of polypropylene (PP)

■Explanation

Original PP and heat treated PP which was held at 230°C for one hour twice were measured. Due to decline of crystallinity, heat melting calorie is down to 94.1% of the original.

■Analytical Conditions

Instrument : DSC-60
Sample : PP
Sample Amount : 5.13mg
Atmospheric Gas : N_2
Flow Rate : 50mL/min
[Temperature Program]
Heating Rate : 10°C/min

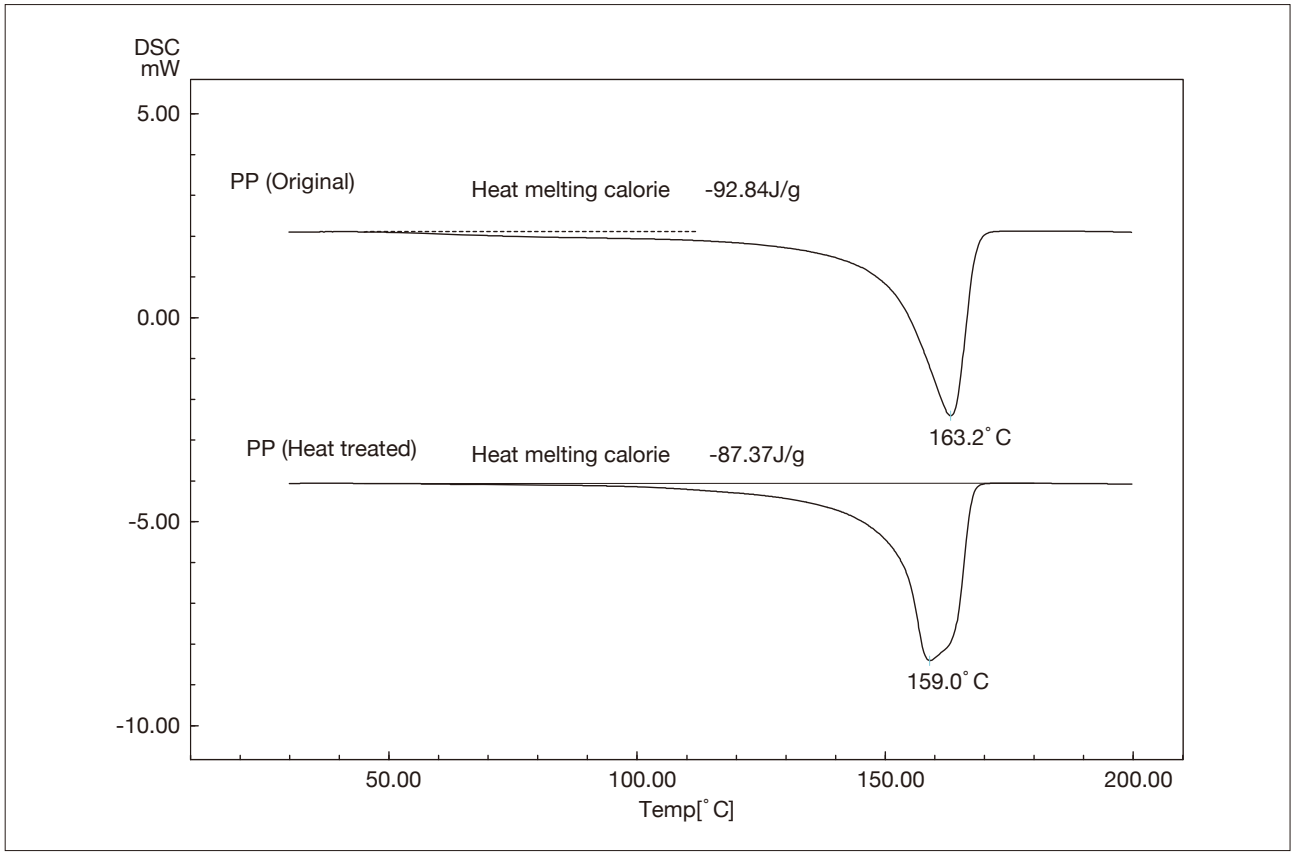


Fig. 2.2.1 DSC curves of PP original and Heat treated PP

2.3 Analysis of mixtured sample of polypropylene (PP) and polyethylene (PE)

■Explanation

DSC melting peak area is proportion to sample amount. In case of mixture, mixing ratio can be measured from each DSC melting peak areas. Each PE and PP sample and the mixture of them were measured.

PE: 439.98 ÷ 132.63 = 3.32mg

PP: 300.70 ÷ 89.81 = 3.35mg

This shows that the mixing ratio is 1:1. The approximate mixing ratio is measured by DSC.

■Analytical Conditions

Instrument	: DSC-60
Sample	: PE-PP mixture sample
Sample Amount	: 6.71mg
Atmospheric Gas	: N_2
Flow Rate	: 50mL/min
[Temperature Program]	
Heating Rate	: 5°C/min

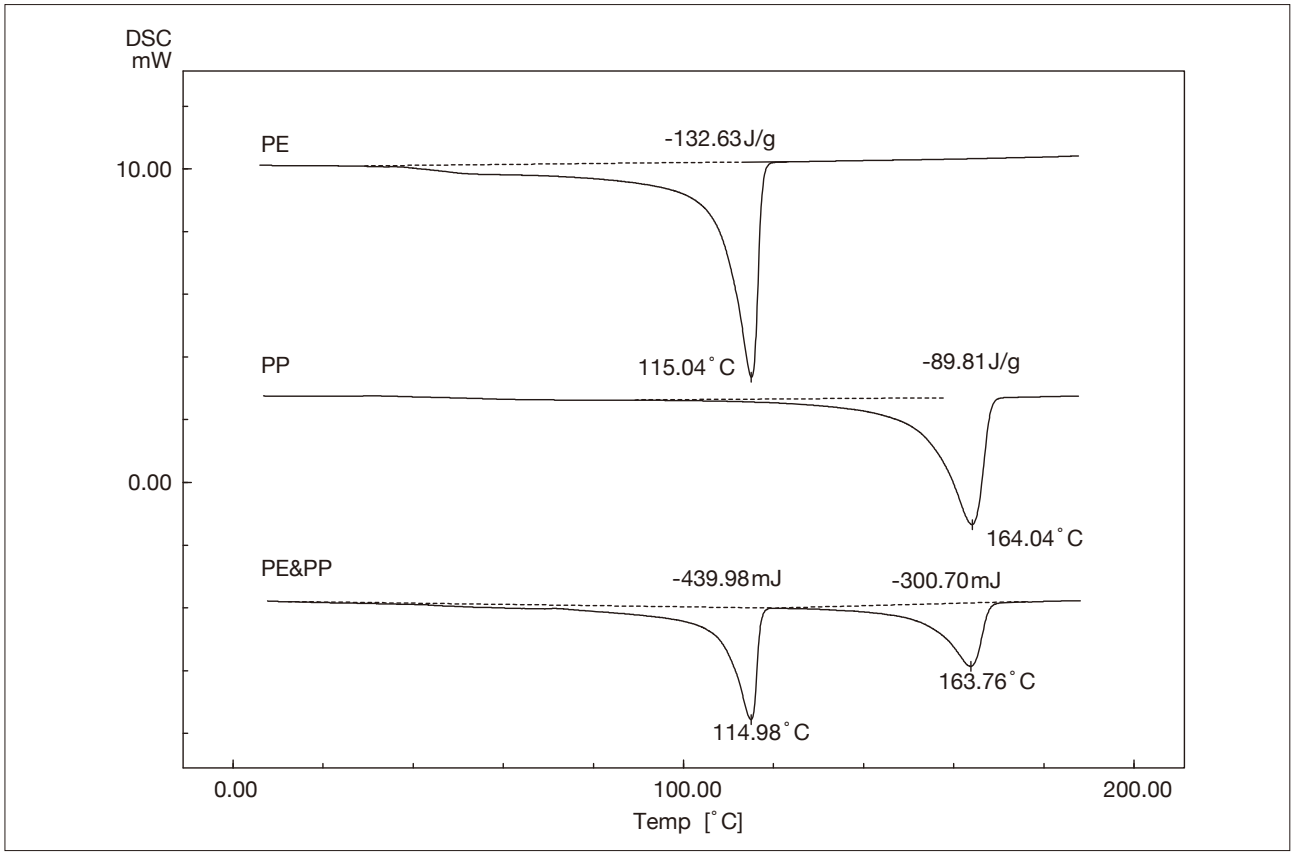


Fig. 2.3.1 DSC curves of PE-PP mixture sample

3 Characterization by Glass Transition

3.1 Glass transition of high-impact polystyrene (PS)

■Explanation

If a non-crystalline high polymer is heated, in order that a high-polymer chain may begin internal rotation at a certain temperature, specific heat will change abruptly. This temperature is called glass transition temperature. Glass transition temperature is characteristic temperature showing the thermal character of a polymer and reflects the molecular structure and the heat history of a sample directly. Here, glass transition of PS and high-impact PS was measured. Glass transition temperature of high-impact PS is falling about 14˚C than that of general PS. Moreover, after heat-treating each sample at 150˚C, when the rapid cooling was carried out, glass transition temperature went up 5-7˚C, respectively.

■Analytical Conditions

Instrument	: DSC-60
Sample	: PS
Sample Amount	: 10.18mg
Sample	: High-impact PS
Sample Amount	: 10.02mg
[Temperature Program]	
Heating Rate	: 20˚C/min

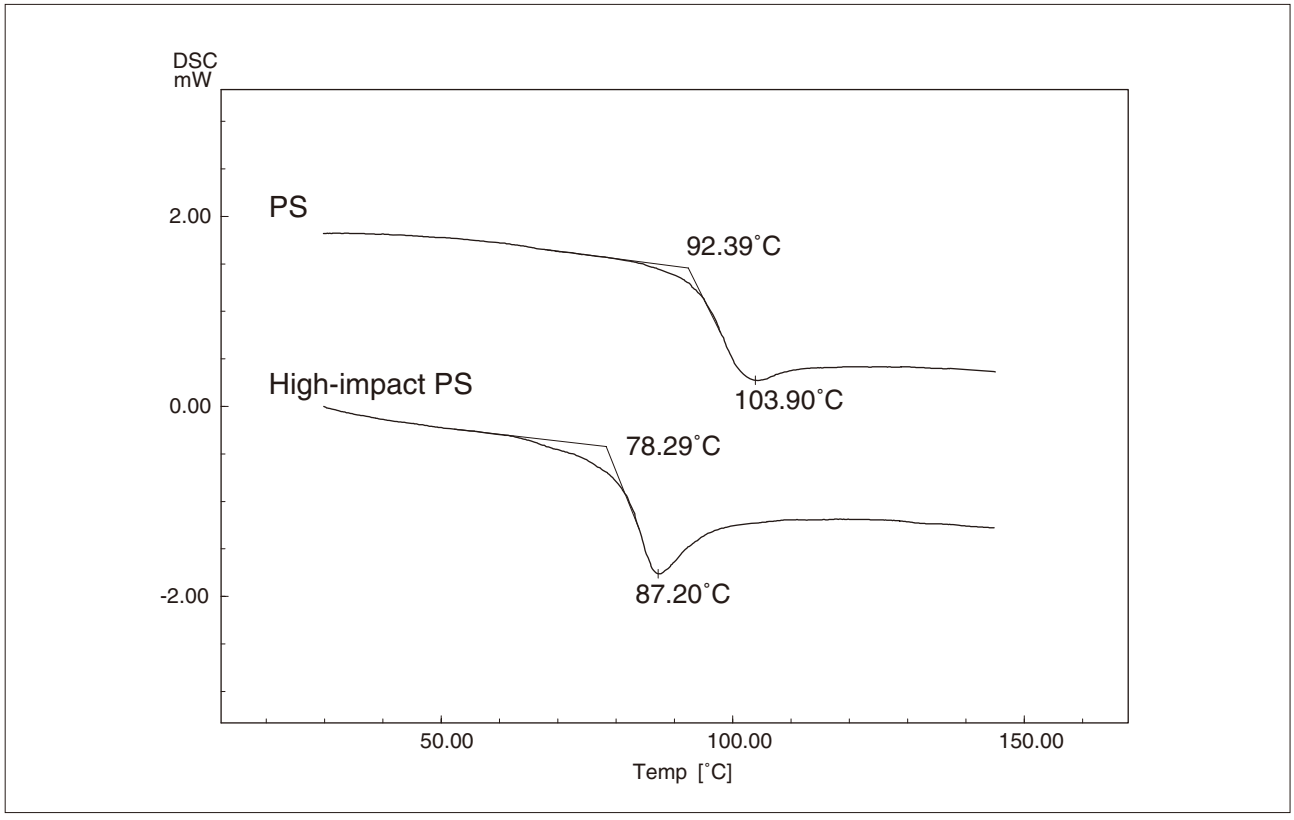


Fig. 3.1.1 DSC curves of PS and High-impact PS

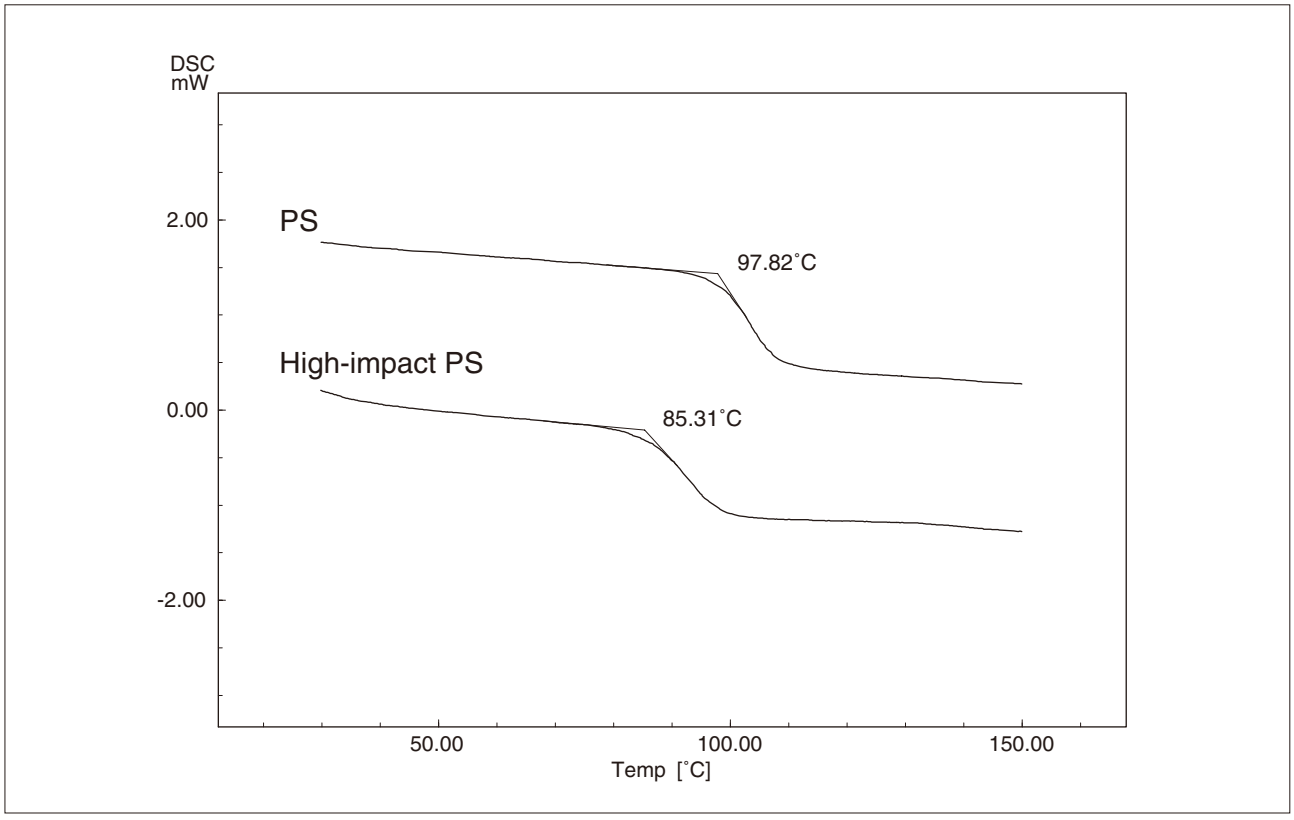


Fig. 3.1.2 DSC curves after heat treatment

3.2 Glass transition of polyvinylchloride (PVC)

■Explanation

Here, the glass transition temperature of PVC which changed the amount of addition of plasticizer was measured.
Sample B has much amount of plasticizer compared with A, and glass transition temperature is low about 7.8˚C.

■Analytical Conditions

Instrument : DSC-60
Sample : PVC(A)
Sample Amount : 10.76mg
Sample : PVC(B)
Sample Amount : 9.77mg
[Temperature Program]
Heating Rate : 20˚C/min

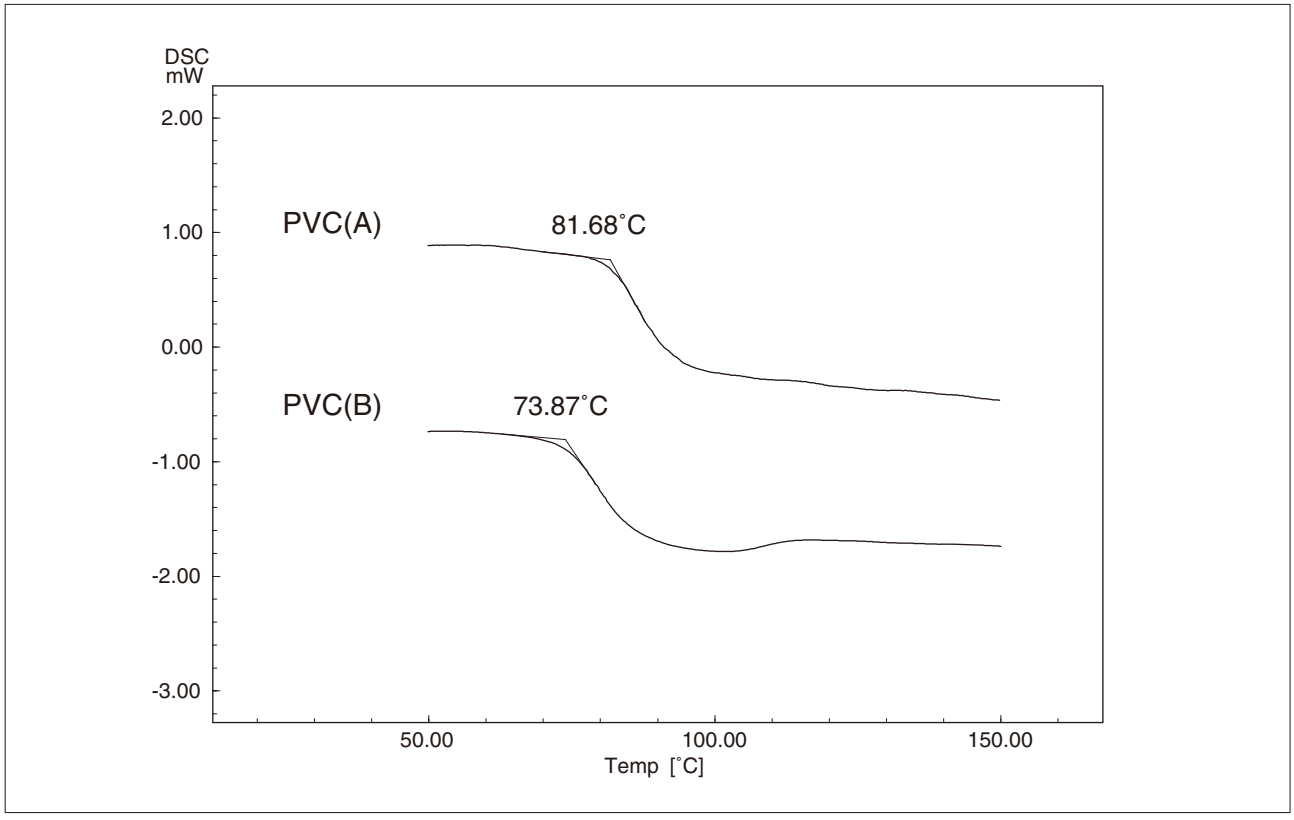


Fig. 3.2.1 DSC curves of PVC

3.3 Glass transition of polyimide (PI)

■Explanation

Glass transition temperature of polyimide is 307.6˚C and high. Curing of unreacted polyimide corresponding to 6.2J/g was detected at 371.4˚C.
Moreover, in second run, glass transition temperature became 314.8˚C and moved to 7.2˚C higher-temperature side.

■Analytical Conditions

Instrument	: DSC-60
Sample	: PI
Sample Amount	: 7.56mg
Atmospheric Gas	: N_2
Flow Rate	: 30mL/min
[Temperature Program]	
Heating Rate	: 20˚C/min

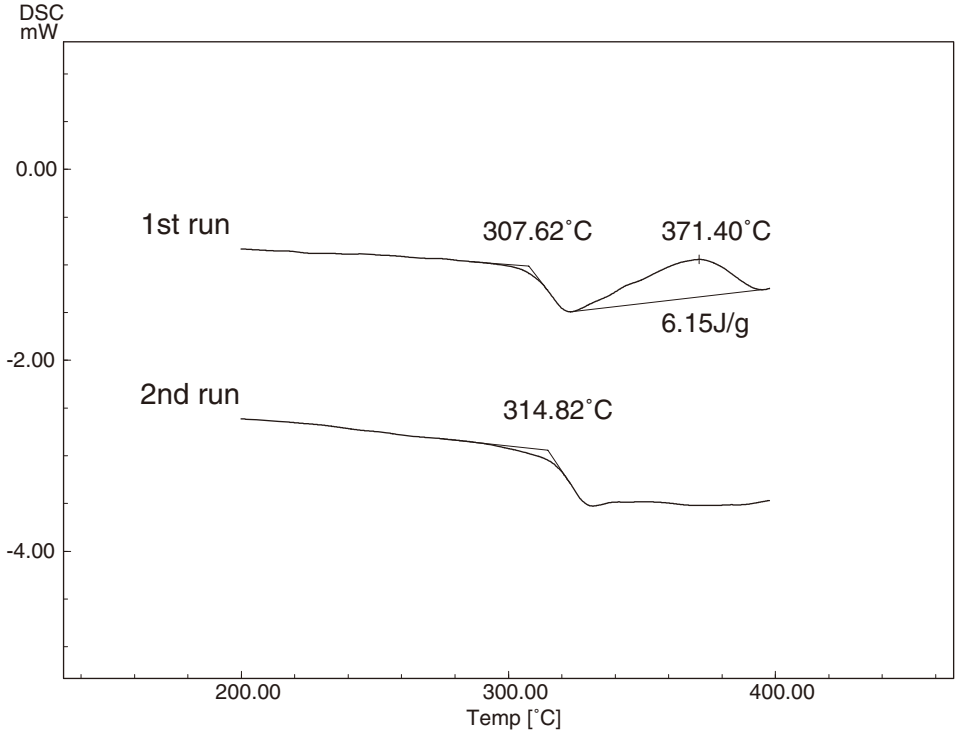


Fig. 3.3.1 DSC curves of Polyimide

4 Measurement of Decomposition and Oxidation Reaction

4.1 Decomposition of nylon 6

■Explanation

Nylon 6 was heated in nitrogen. On DTA curve, a endothermic peak at 222˚C corresponds to melting and a endothermic peak at 447.3˚C corresponds to decomposition reaction.
The endothermic change after 500˚C is also a de-composition reaction.
Moreover, the very small weight loss seen by 200˚C on TG curve is caused by dehydration.
The weight loss by decomposition is measured after that.

■Analytical Conditions

Instrument : DTG-60
Sample : nylon 6
Sample Amount : 9.43mg
Atmospheric Gas : N_2
[Temperature Program]
Heating Rate : 10˚C/min

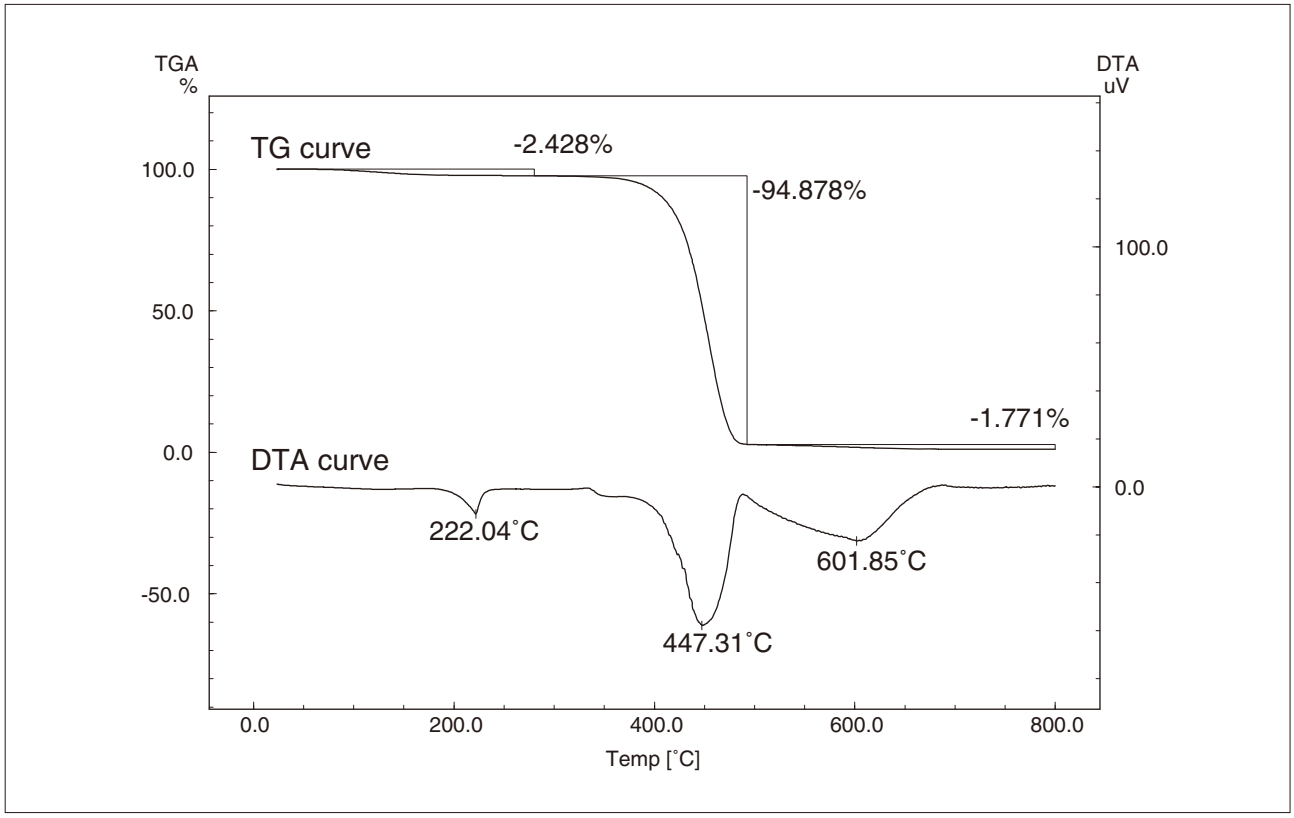


Fig. 4.1.1 TG-DTA curves of nylon 6

4.2 Decomposition characteristic of modified polyphenyleneoxide (PPO)

■Explanation

Measurement of the decomposition process by TGA is performed to evaluate the thermal resistance property of a sample by thermal analysis.
Performs the measurement raising temperature at constant rate, and finds the start temperature of decomposition and the ratio of decomposition.
Here, modified PPO was measured.
Seemingly, it turns out that decomposition has started from near 300˚C.
Moreover, the progress degree of the decomposition reaction at constant temperature can also be measured directly.
Here, the decomposition process when holding at 300˚C was measured.

■Analytical Conditions

Instrument	: TGA-50
Sample(Fig.4.2.1)	: modified PPO
Sample Amount(Fig.4.2.1)	: 12.05mg
Sample(Fig.4.2.2)	: modified PPO
Sample Amount(Fig.4.2.2)	: 11.6mg
Atmospheric Gas	: N_2
Flow Rate	: 30mL/min
[Temperature Program]	
Heating Rate(Fig.4.2.1)	: 10˚C/min
Holding Temperature(Fig.4.2.2)	: 300˚C

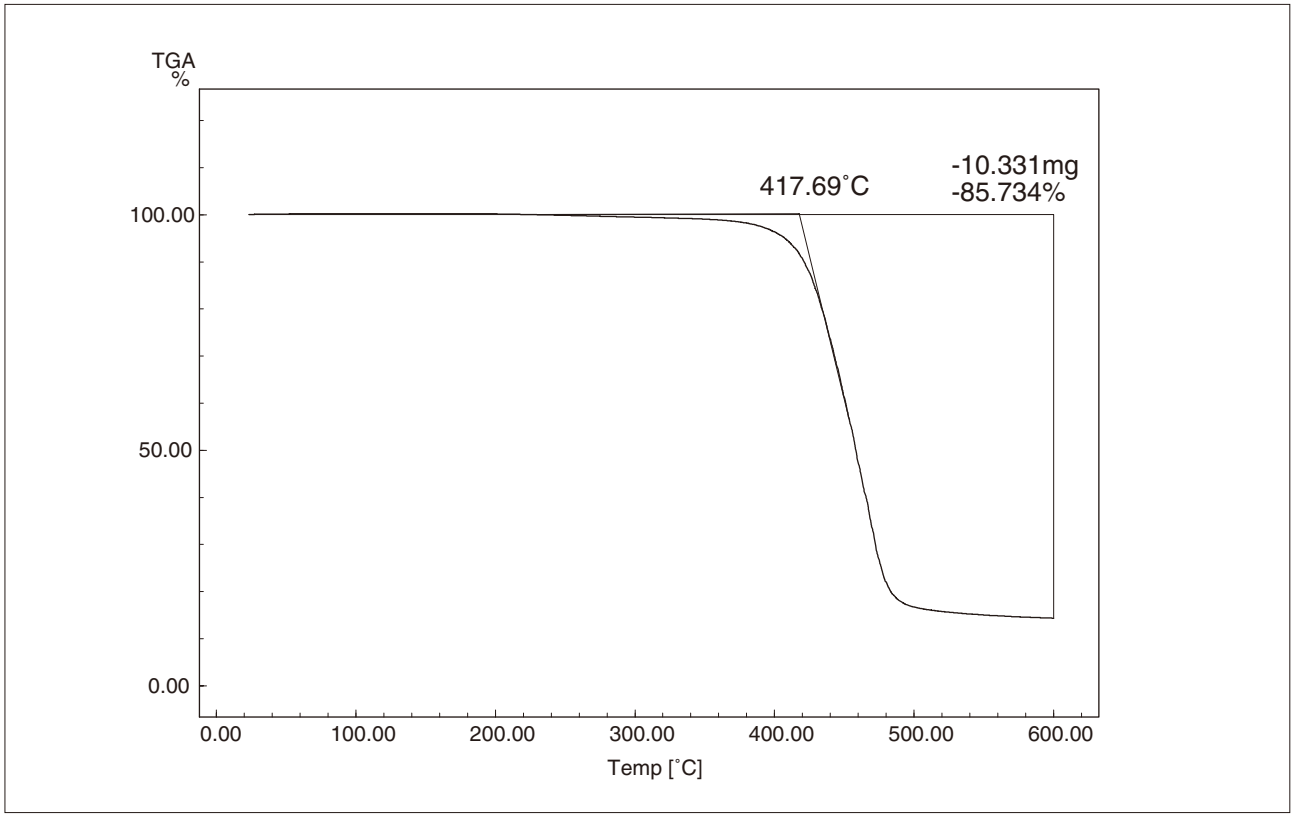


Fig. 4.2.1 TG curve of modified PPO

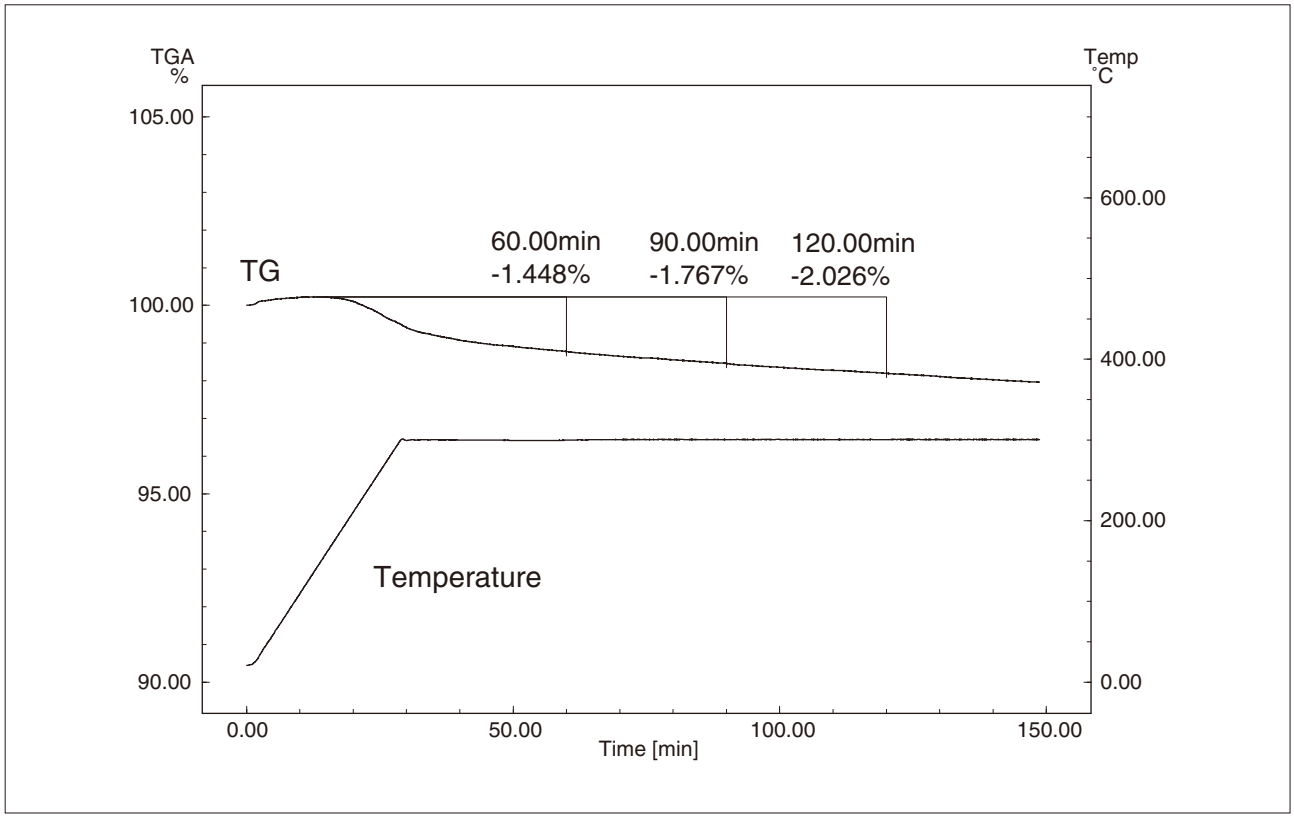


Fig. 4.2.2 TG curve of modified PPO (Isothermal)

4.3 Decomposition of polyethyleneterephthalate (PET)

■Explanation

Here, PET was measured.
Seemingly, it turns out that decomposition has started from near 350˚C.
Moreover, it turns out that decomposition is proceeding also at a low temperature of 280˚C.

■Analytical Conditions

Instrument	: TGA-50
Sample(Fig.4.3.1)	: PET
Sample Amount(Fig.4.3.1)	: 10.71mg
Sample(Fig.4.3.2)	: PET
Sample Amount(Fig.4.3.2)	: 11.32mg
Atmospheric Gas	: N_2
Flow Rate	: 30mL/min
[Temperature Program]	
Heating Rate(Fig.4.3.1)	: 10˚C/min
Holding Temperature(Fig.4.3.2)	: 280˚C

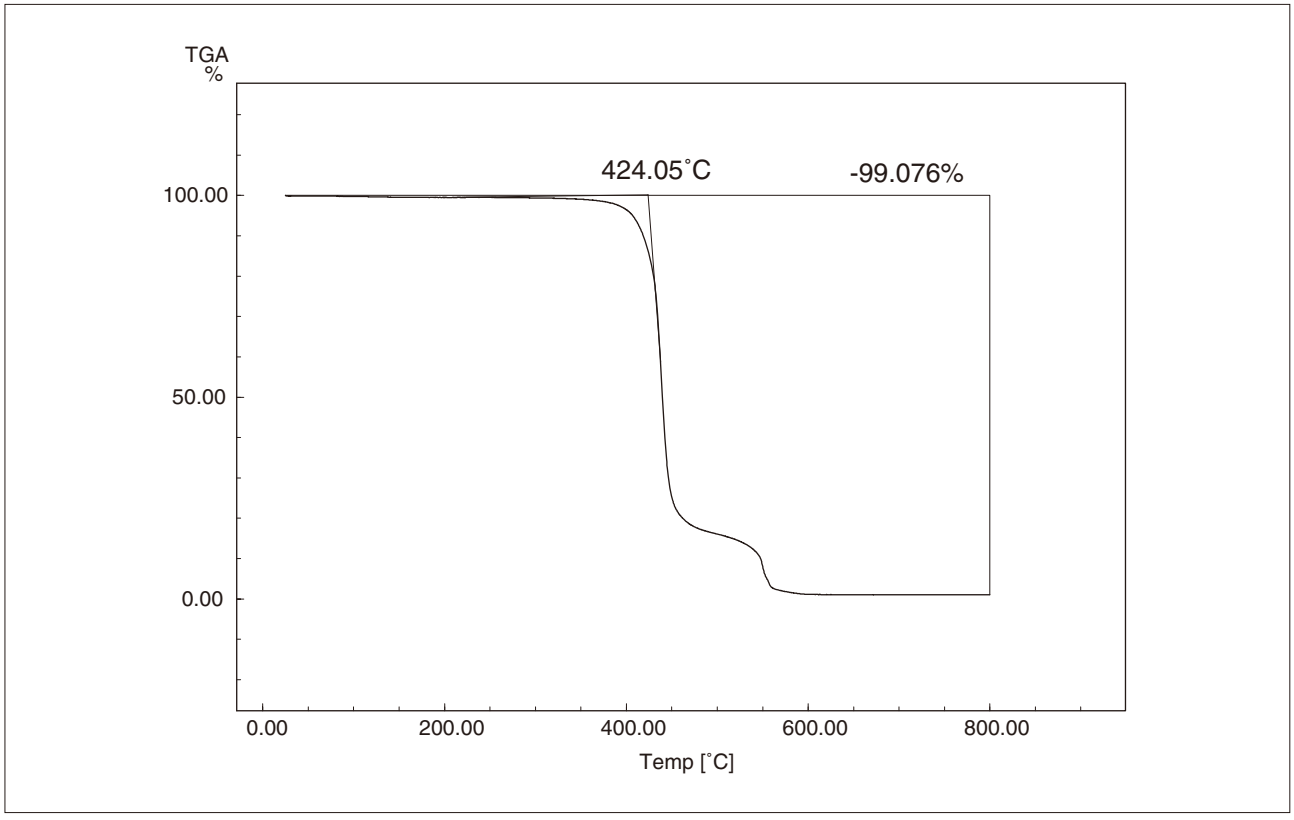


Fig. 4.3.1 Programmed Thermal Decomposition of PET

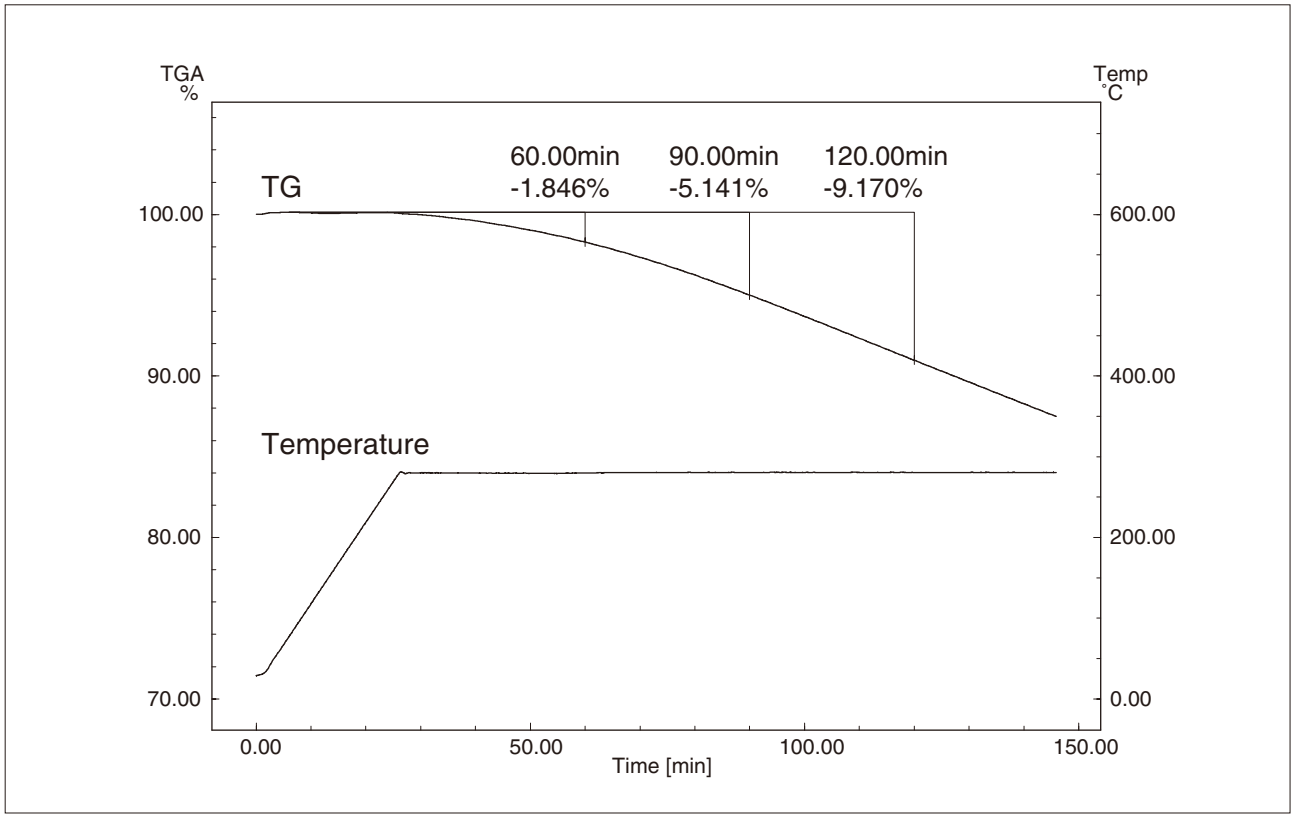


Fig. 4.3.2 Isothermal Decomposition of PET

4.4 Oxygen induction time (OIT) of polyethylene (PE)

■Explanation

PE is used for covering of an electric wire. However, by using it for a long period of time, oxygen in air is absorbed and it deteriorates gradually. The anti-oxidant is added in PE in order to prevent this oxidation reaction.
This effect can be investigated by measuring oxygen induction time (OIT) using DSC.
A sample is heated in nitrogen to the temperature to measure, and after reaching a purposed temperature, atmospheric gas is changed to oxygen. The time from inducing oxygen to the beginning of the exothermic peak by oxygen absorption is measured. Here, when held at 190˚C, oxygen induction time was 78.58 minutes, and when held at 200˚C it became 20.46 minutes.

■Analytical Conditions

Instrument	: DSC-60
Software	: OIT
Sample	: PE
Sample Amount(Fig.4.4.1)	: 5.05mg
Sample Amount(Fig.4.4.2)	: 5.05mg
Atmospheric Gas	: $N_2 \rightarrow O_2$
Flow Rate	: 50mL/min
[Temperature Program]	
Holding Temperature(Fig.4.4.1)	: 190˚C
Holding Temperature(Fig.4.4.2)	: 200˚C

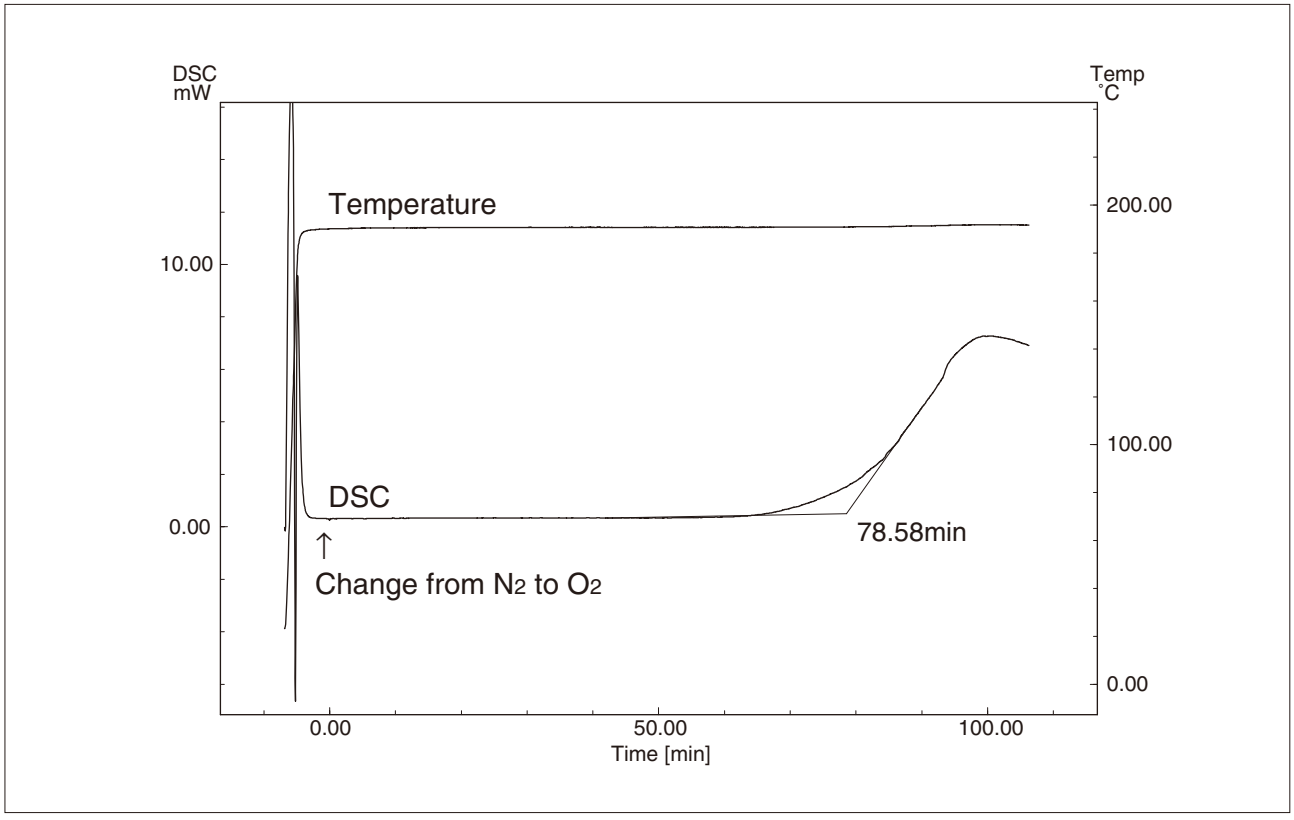


Fig. 4.4.1 Oxygen induction time of PE at 190˚C

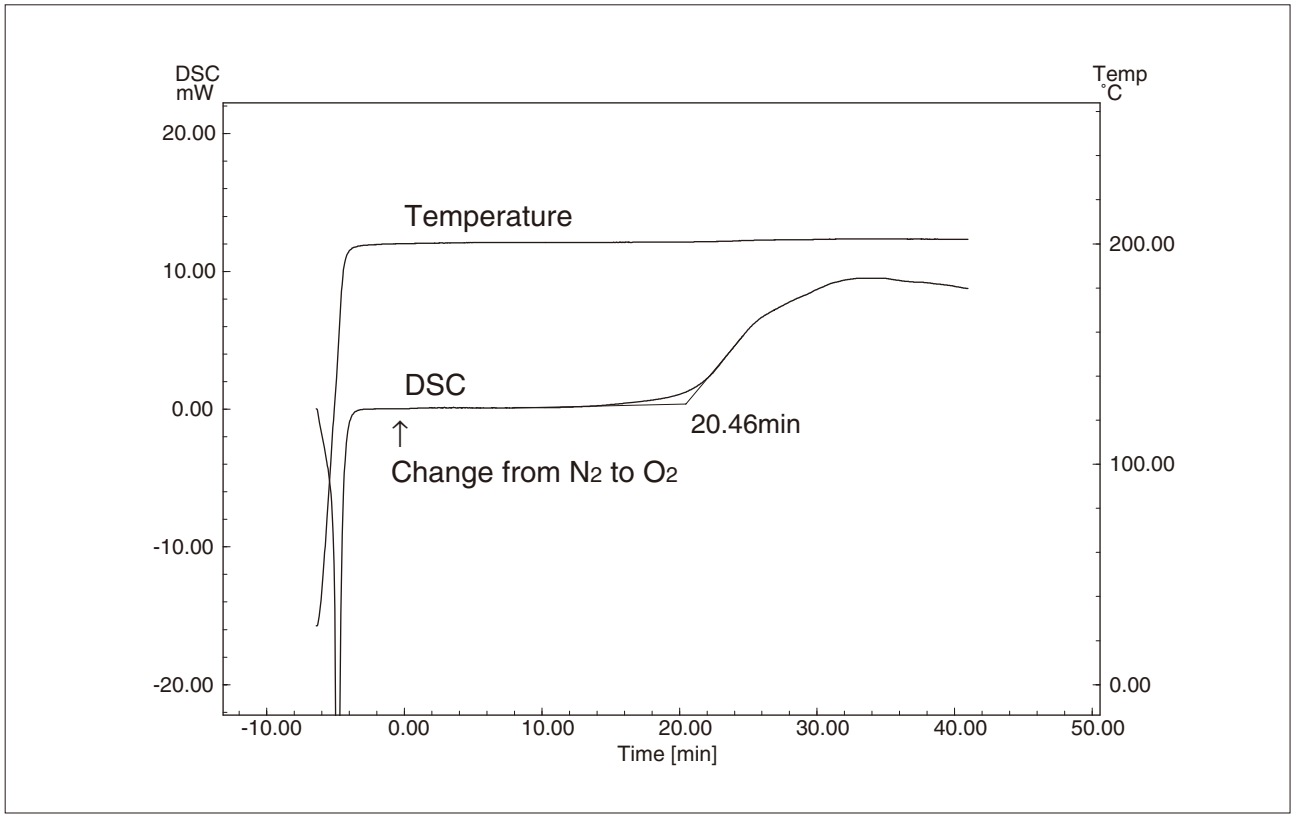


Fig. 4.4.2 Oxygen induction time of PE at 200°C

4.5. Thermal decomposition of Fluororesin

■Explanation

Thermal decomposition measurement of Fluororesin which generates reactive gas was performed.

■Analytical Conditions

Instrument : TGA-50
Sample : Fluororesin
Sample Amount : 24.47mg
Atmospheric Gas : Air
Flow Rate : 40mL/min
[Temperature Program]
Heating Rate : 10˚C/min

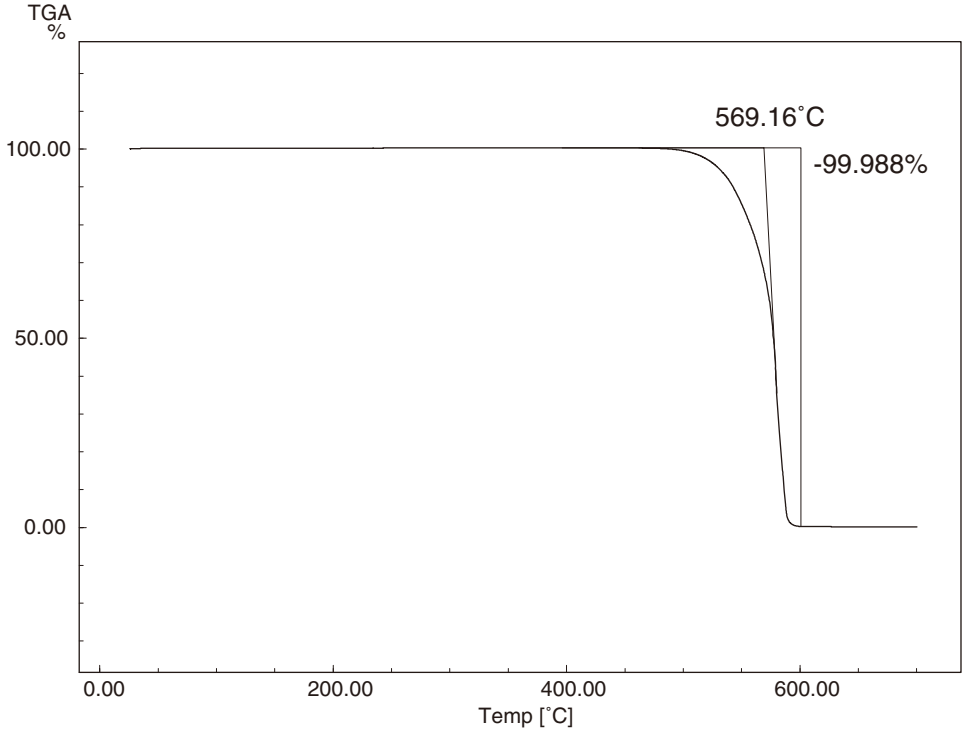


Fig. 4.5.1 TG curve of Fluororesin

5 Condensation Reaction of Phenol Resin

5.1 Condensation reaction of phenol resin

■Explanation

Evaporation of water needs to be prevented in the calorimetric measurement of a condensation reaction. Since a reaction occurs at high temperature of 169°C, it was measured using the high pressure cell (hermetic crucible). Glass transition was found at 70.9°C.

■Analytical Conditions

Instrument	: DSC-60
Sample	: Phenol Resin
Sample Amount	: 3.44mg
Cell	: Aluminium high pressure cell
Atmospheric Gas	: N_2
Flow Rate	: 30mL/min
[Temperature Program]	
Heating Rate	: 10°C/min

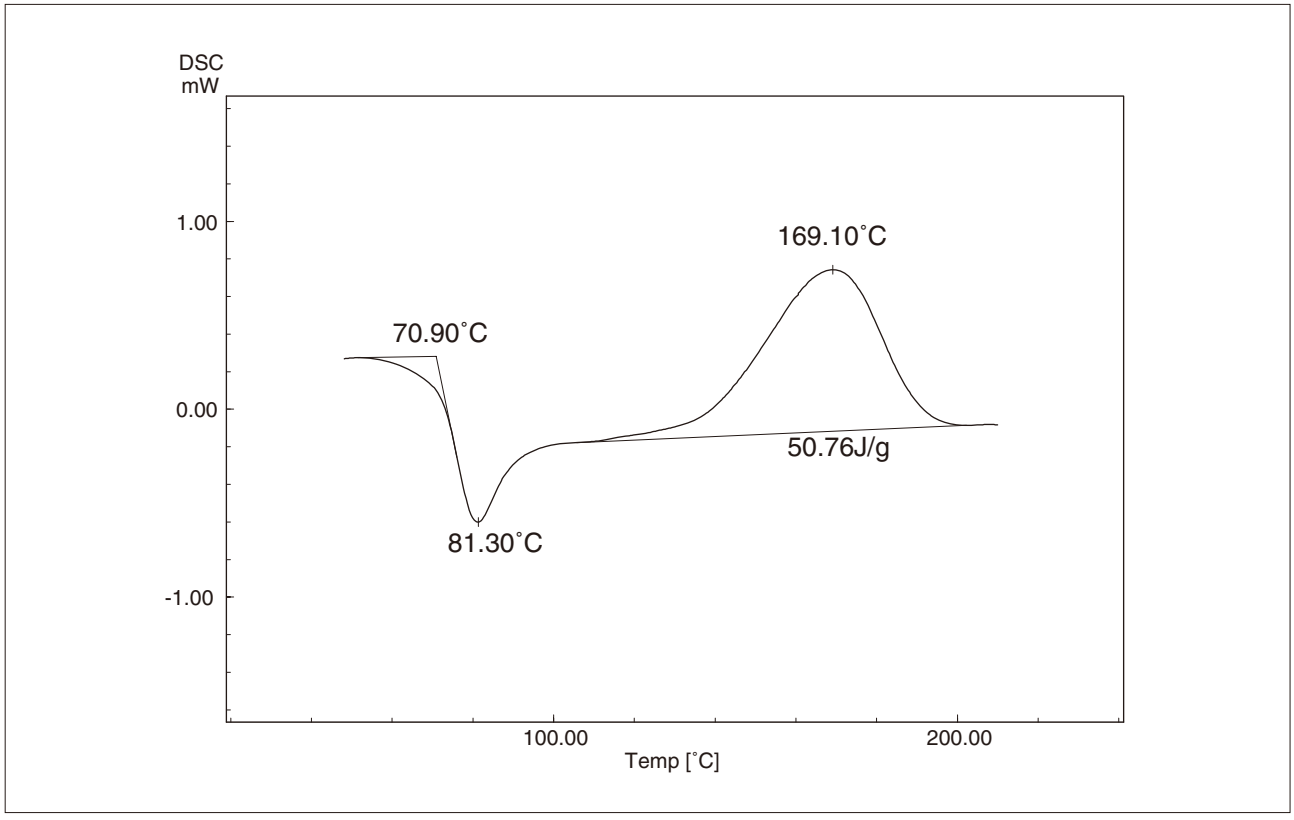


Fig. 5.1.1 DSC curve of Phenol Resin

6 Quantification of Reinforcing Materials

6.1 Quantification of glass fiber in polyethyleneterephthalate (PET)

■Explanation

Inorganic reinforcing materials are added for the improvement of mechanical strength and heat resistance. If the sample is heated in air using TG, this quantity can be measured easily.

TG curve shows that decomposition starts from near 400˚C,and ends near 650˚C. During this period, PET decomposes completely, and inorganic residue remains. Therefore, the quantity that deducted the amount of decomposition of PET from the amount of original sample becomes the amount of glass fiber.

(100-65.85=34.15%)

■Analytical Conditions

Instrument	: TGA-50
Sample	: PET
Sample Amount	: 11.19mg
Atmospheric Gas	: Air
Flow Rate	: 30mL/min
[Temperature Program]	
Heating Rate	: 50˚C/min

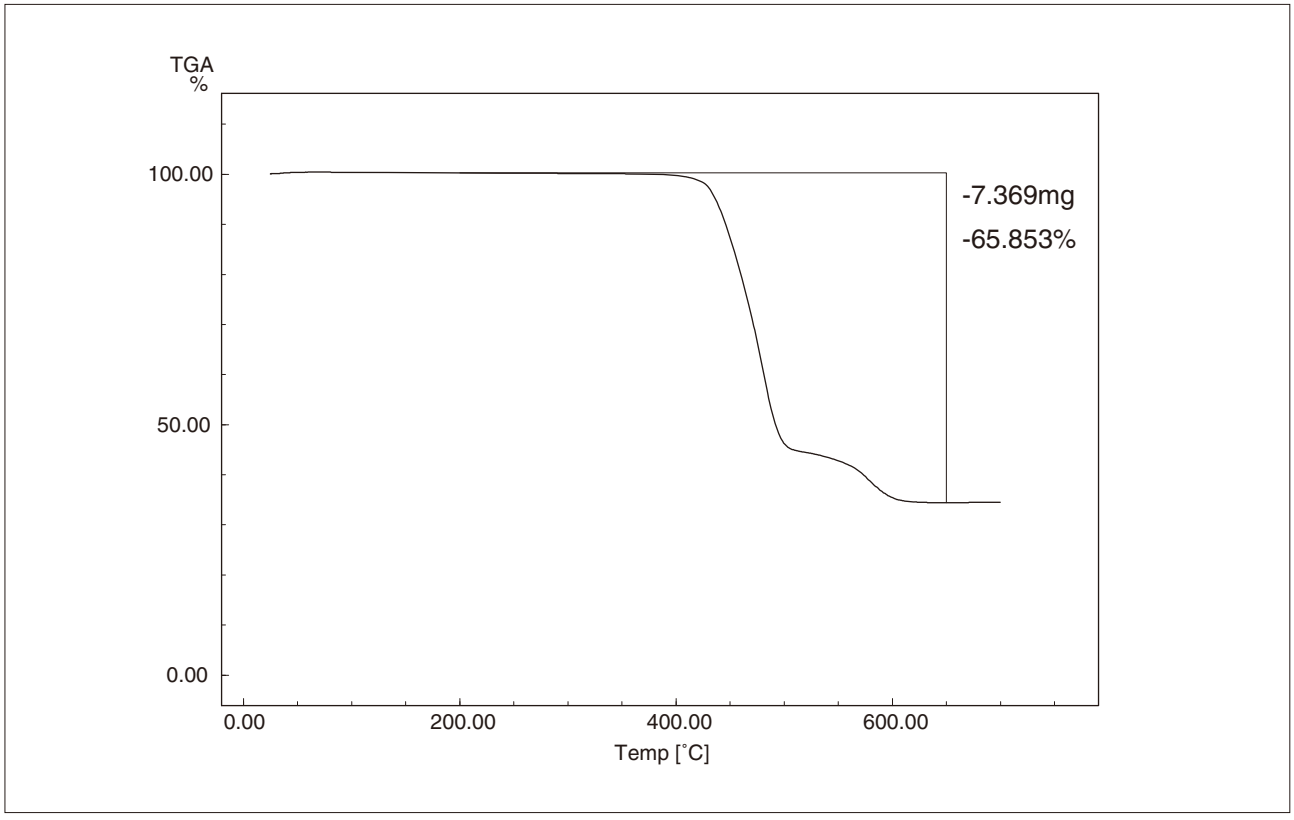


Fig. 6.1.1 TG curve of PET

6.2 Quantification of carbon black in styrene-butadiene rubber (SBR)

■Explanation

In DTG, quantification is performed by heating, controlling atmosphere. After setting a sample to equipment first, atmosphere is replaced with nitrogen enough. If a sample is heated to about 600˚C, the weight loss by thermal decomposition of SBR will be observed by TG. If atmosphere is changed to air after SBR decomposes completely, the weight loss by oxidation of carbon black will be observed shortly. Quantified value became 28.2%. In DTA, the endothermic peak by decomposition of SBR and the exothermic peak by oxidation of carbon black are observed.

■Analytical Conditions

Instrument : DTG-60
Sample : SBR
Sample Amount : 20.19mg
Atmospheric Gas : $N_2 \rightarrow$Air
[Temperature Program]
Heating Rate : 20˚C/min

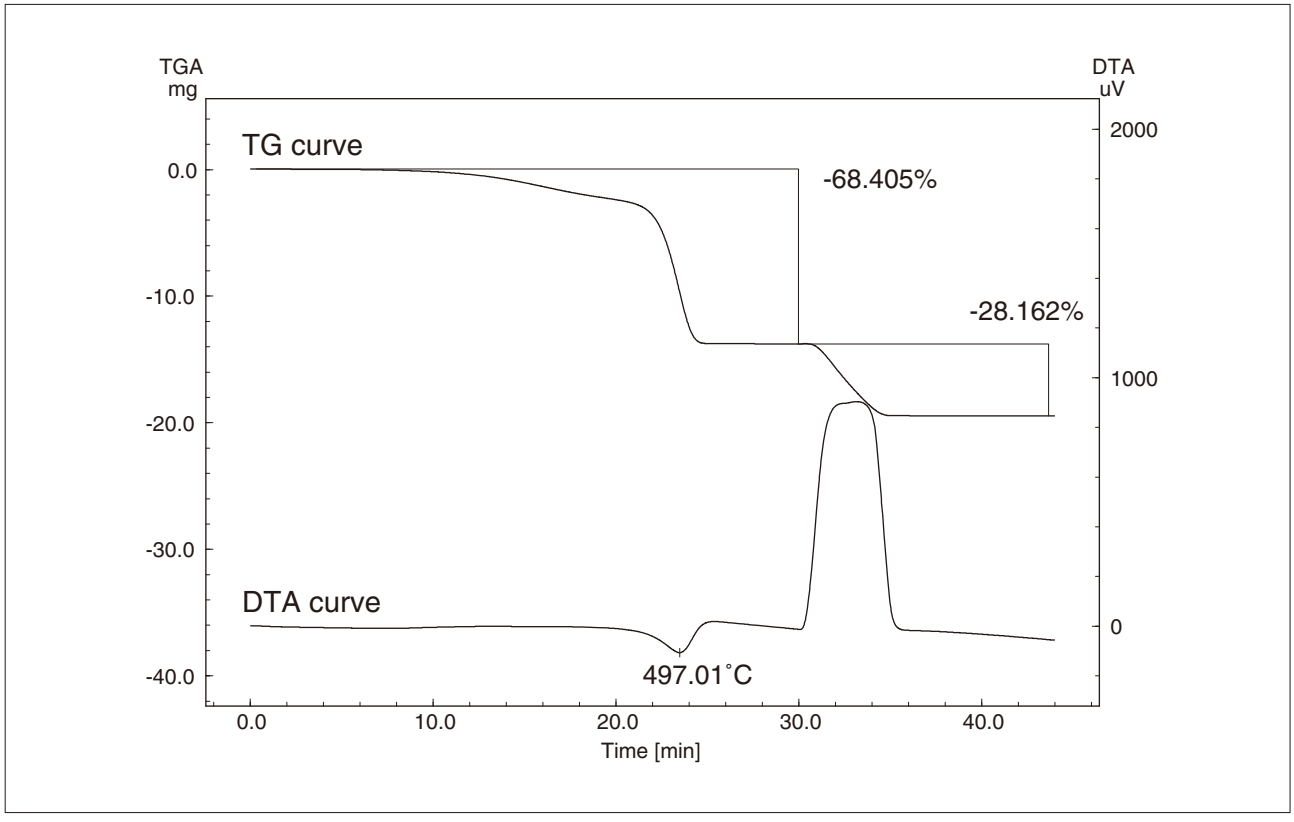


Fig. 6.2.1 TG-DTA curves of SBR

7 Electronic Materials

7.1 Decomposition of a diode

■Explanation

The diode of semiconductor parts was measured.
A part of component which constitutes the diode is melting near 225˚C, and decomposition has started from near 300˚C.

■Analytical Conditions

Instrument	: DTG-60
Sample	: Diode
Sample Amount	: 10.1mg
Atmospheric Gas	: Air
[Temperature Program]	
Heating Rate	: 10˚C/min

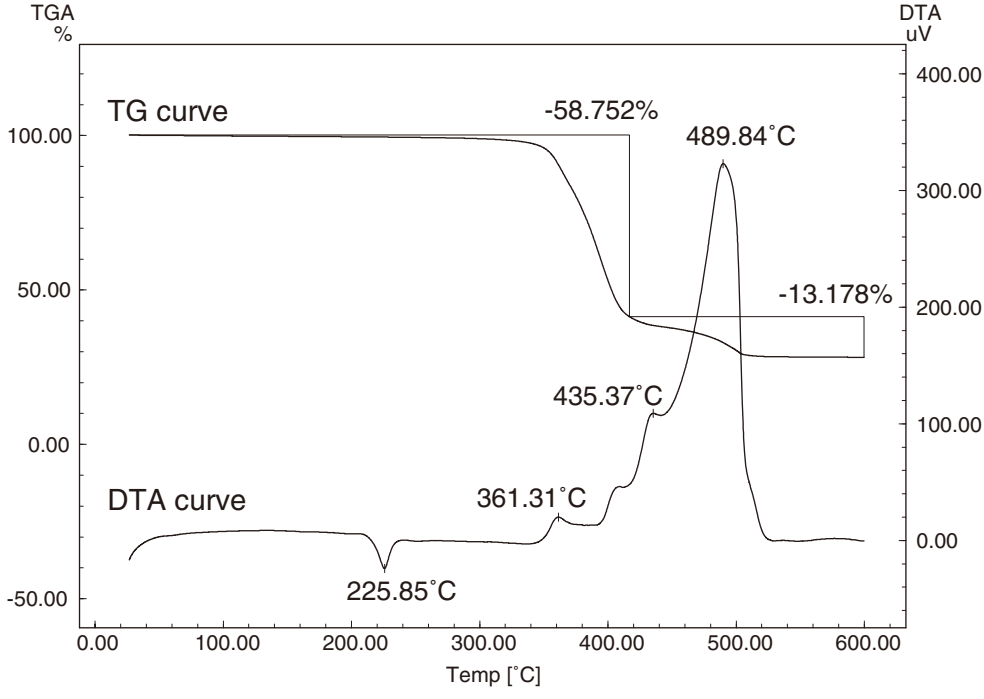


Fig. 7.1.1 TG-DTA curves of a Diode

7.2 Quantification of quartz in epoxy resin

■Explanation

Here, the epoxy resin was heated in air.
TG shows that decomposition starts from near 300˚C, and ends near 550˚C.
During this period, epoxy resin decomposes completely, and inorganic residue remains. Therefore, the quantity that deducted the amount of decomposition of epoxy resin from the amount of original sample becomes amount of filling of quartz. (100-33.8=66.2%)Moreover, in DTA, glass transition of epoxy resin at 85˚C is measured, and in 300-550˚C, endothermic and exothermic peaks corresponding to decomposition are measured.
Furthermore, a trace endothermic peak at 580˚C corresponds to transition of quartz.

■Analytical Conditions

Instrument	: DTG-60
Sample	: Epoxy resin
Sample Amount	: 22.67mg
Atmospheric Gas	: Air
Flow Rate	: 150mL/min
[Temperature Program]	
Heating Rate	: 20˚C/min

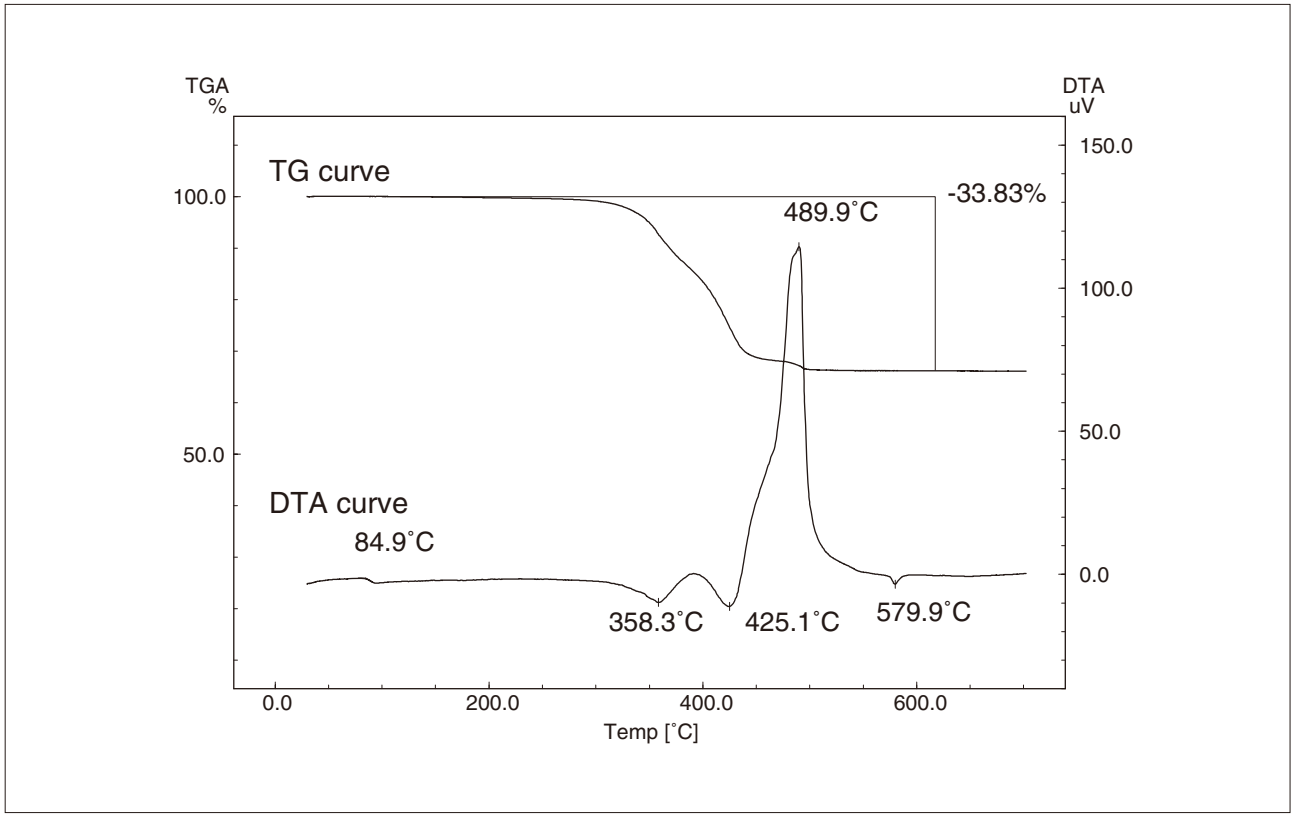


Fig. 7.2.1 Quantification of quartz in epoxy resin

7.3 Melting point of lead free solder

■Explanation

Development of the lead free solder that does not contain a lead from the problem of the environmental pollution is performed.
Here, melting point of the lead free solder with which the conventional Sn-Pb solder differs from composition ratio of components was measured.
Although, as for the solder containing a lead, melting was observed at 182.3˚C, with lead free solder, melting was observed at 209.2˚C and 217.5˚C.

■Analytical Conditions

Instrument : DSC-60
Sample (Fig.7.3.1) : Solder
Sample Amount : 11.26mg
Sample (Fig.7.3.2) : Lead free solder
Sample Amount : 10.38mg
Sample (Fig.7.3.3) : Lead free solder
Sample Amount : 10.71mg
Atmospheric Gas : N_2
[Temperature Program]
Heating Rate : 10˚C/min

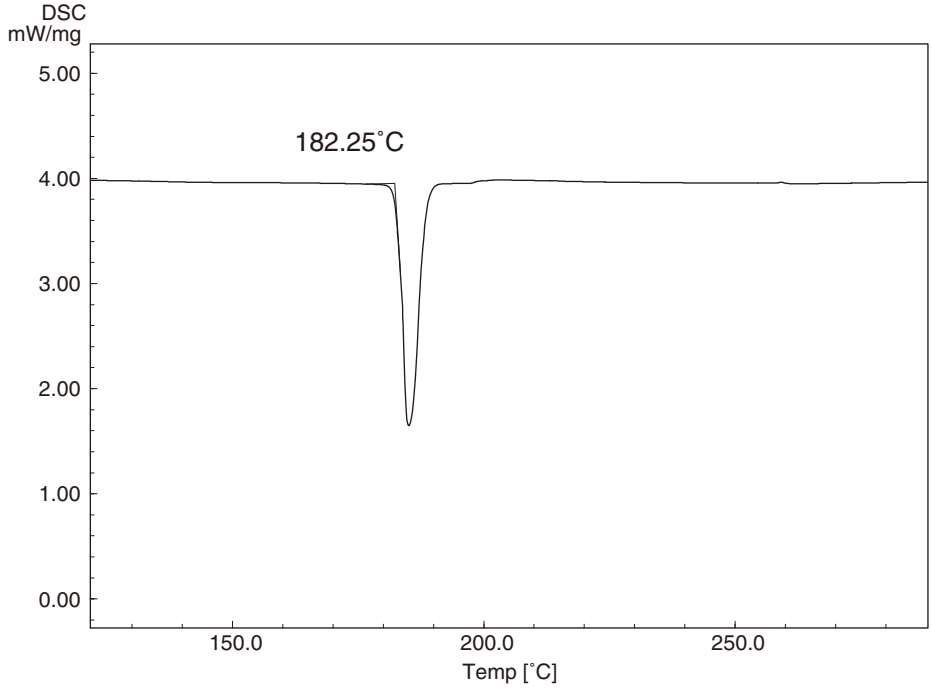


Fig. 7.3.1 DSC curve of Sn–Pb solder

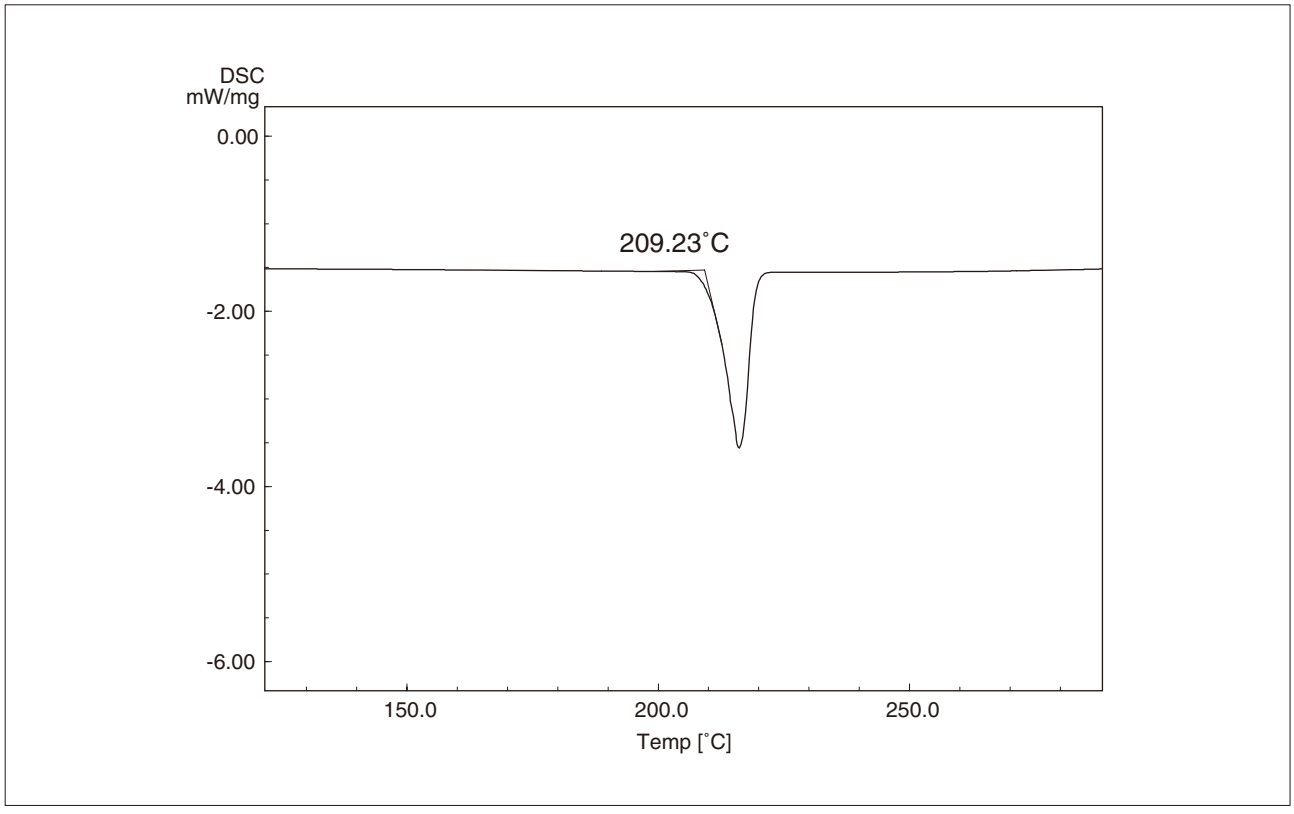


Fig. 7.3.2 DSC curve of lead free solder(Sn–Ag–Bi–Cu)

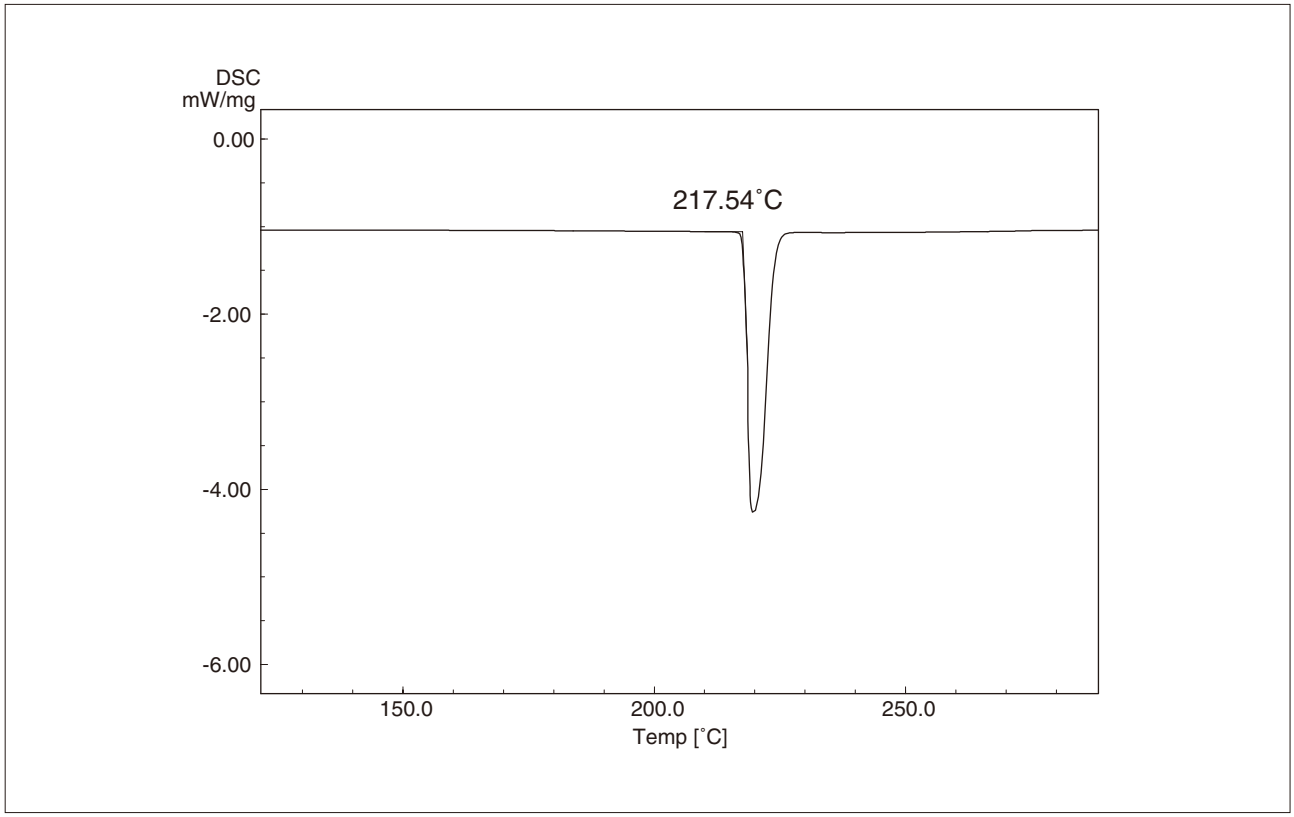


Fig. 7.3.3 DSC curve of lead free solder (Sn–Ag–Cu)

8 Battery Materials

8.1 Analysis of lithium-ion battery separator

■Explanation

Lithium-ion battery separator prevents circuit shortage between positive and negative electrodes, and when the cell gets abnormally heated, it stops passage of lithium-ion. Measuring melting characteristic of lithium-ion battery separator is very important to ensure safety. Three kinds of separators melting were measured by DSC. All of them seemed to be polyethylene from the point of melting temperature. Polyethylene "a" is the lowest, and "b" seems to be mixed with polypropylene because there was another peak around 160°C. Comparing with each amount of heat melting, they shows a<b<c, and the degree of crystallinity is expected with the same order.

■Analytical Conditions

Instrument	: DSC-60
Sample	: Separator "a", "b", "c"
Sample Amount	: 2.0mg
Atmospheric Gas	: N_2
Flow Rate	: 50mL/min
[Temperature Program]	
Heating Rate	: 10°C/min

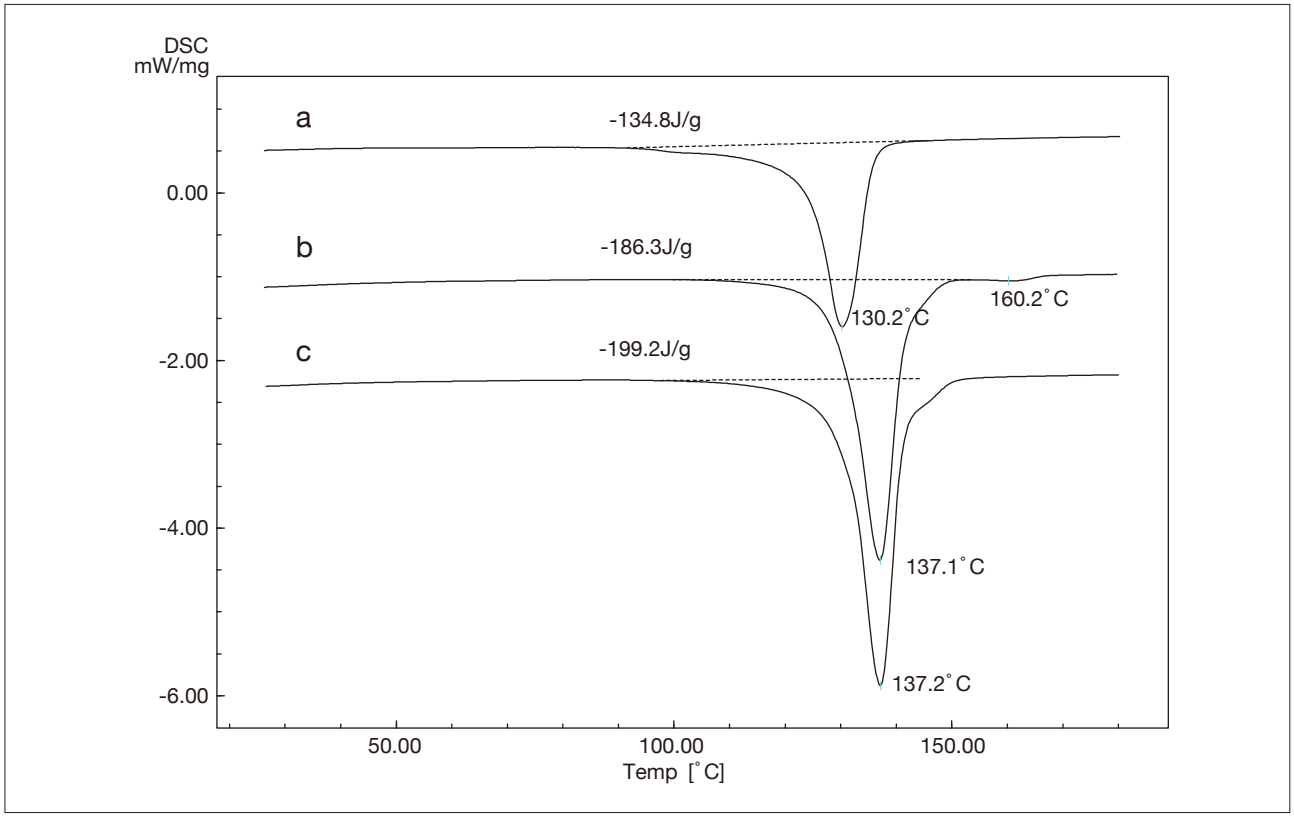


Fig. 8.1.1 DSC curves of Lithium-ion battery separator

8.2 Analysis of film for polymer fuel cell

■Explanation

The film for polymer fuel cell such as Nafion® membrane has clustering structure. The principle of this cell is that movement of the proton in the water in clustering structure makes electricity. Power efficiency depends on the size of cluster because of the volume of containing water. When the wet Nafion® membrane was heated from minus temperature level, some water melt in lower temperature except of free water which melt at 0°C. This water is thought as “water cluster”.

It is thought that the area of melting peak correlate closely with amount of water in a cluster, and temperature correlate closely with the size of average diameter of cluster. DSC enables to get the information about sample structure to analyze melting of ice in sample.

■Analytical Conditions

Instrument	: DSC-60
Sample	: Film for polymer fuel cell
Sample Amount	: 12.0mg
Atmospheric Gas	: N_2
Flow Rate	: 50mL/min
[Temperature Program]	
Heating Rate	: 1°C/min

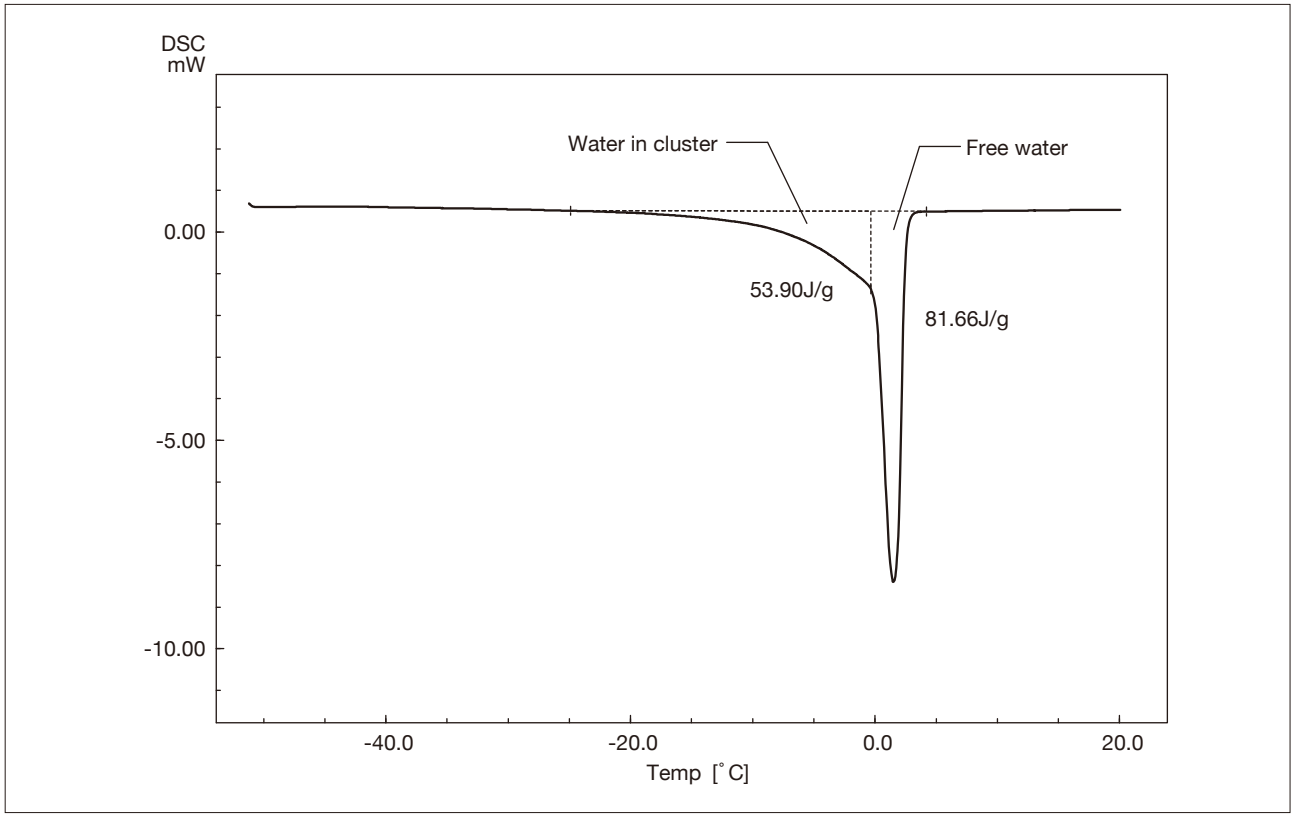


Fig. 8.2.1 DSC curve of film for polymer fuel cell

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