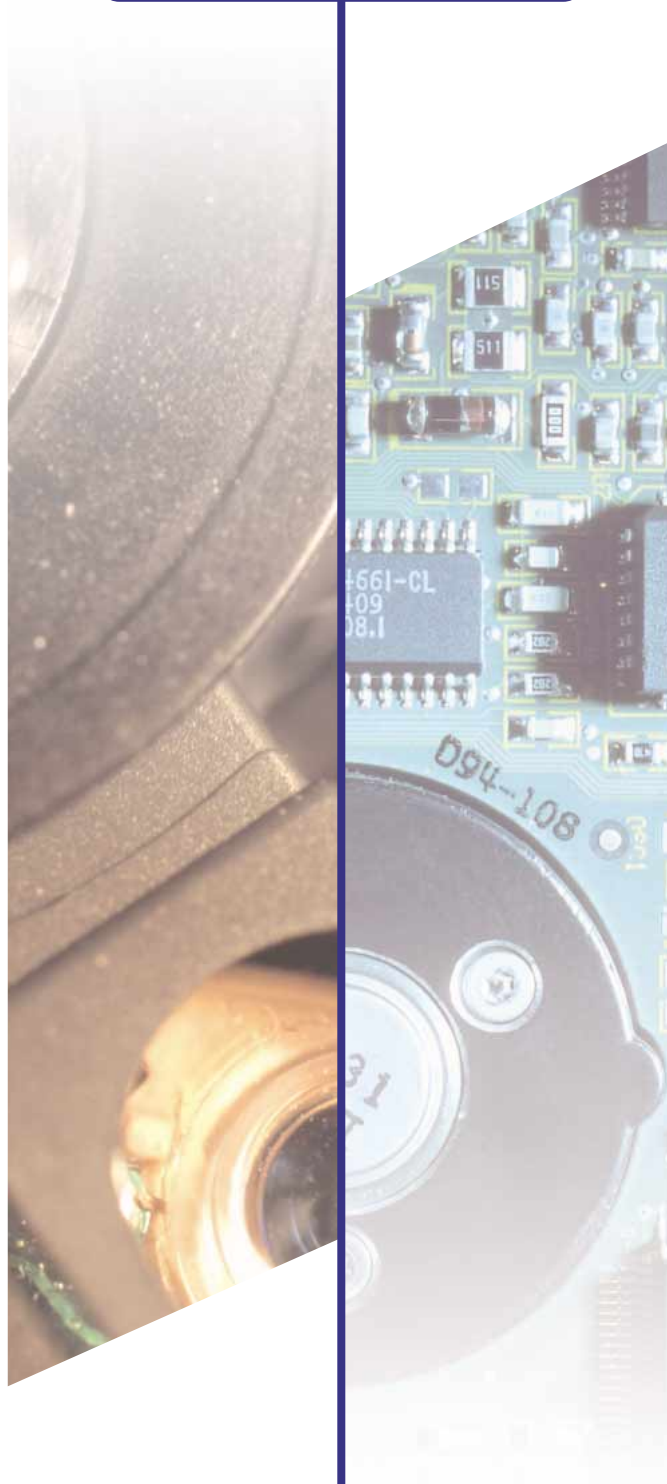


# Thermal Analysis 60 Series Application Data Book

Polymer and Electronic Material



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# 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<sub>2</sub>  
Flow Rate : 50mL/min  
[Temperature Program]  
Heating Rate : 10°C/min

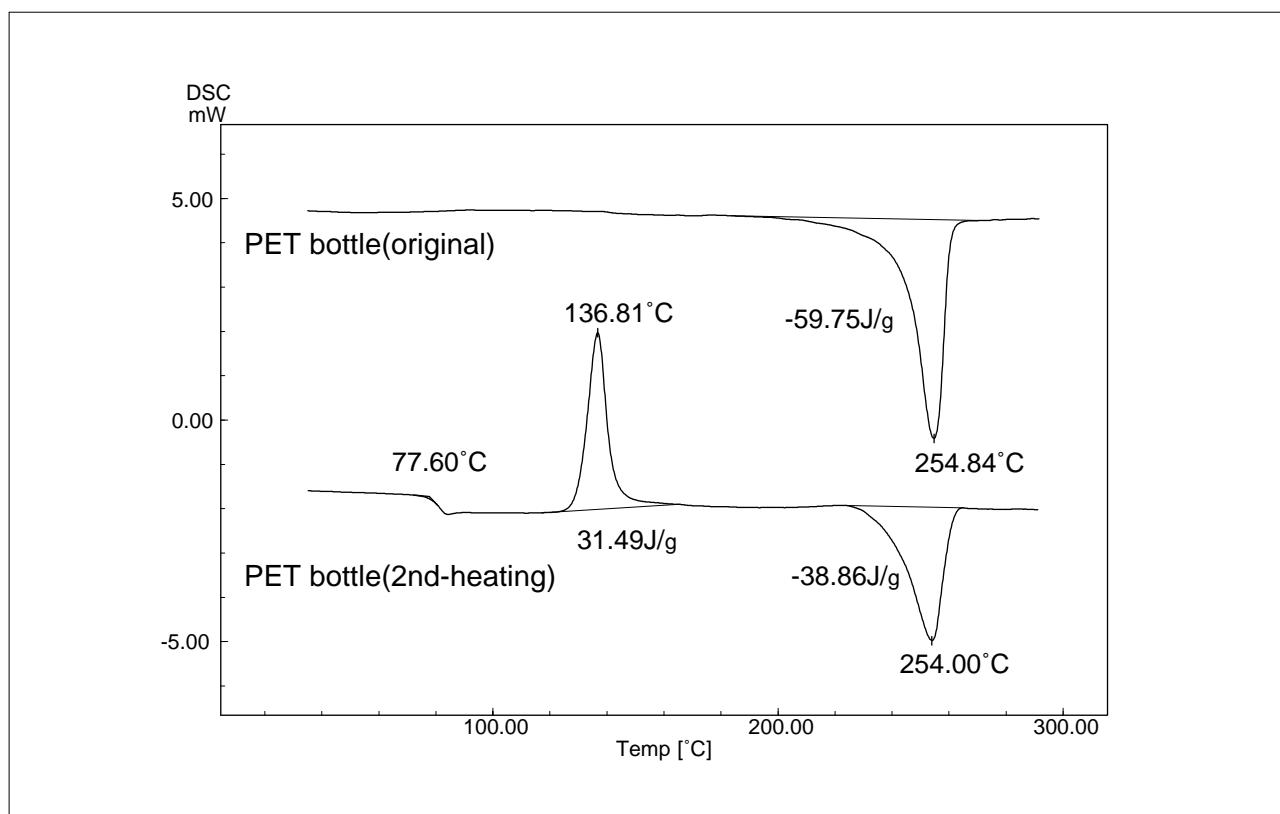


Fig. 1.1.1 DSC curves of PET bottle (original and 2nd-heating)

## 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<sub>2</sub>  
Flow Rate : 50mL/min  
[Temperature Program]  
Heating Rate : 20°C/min

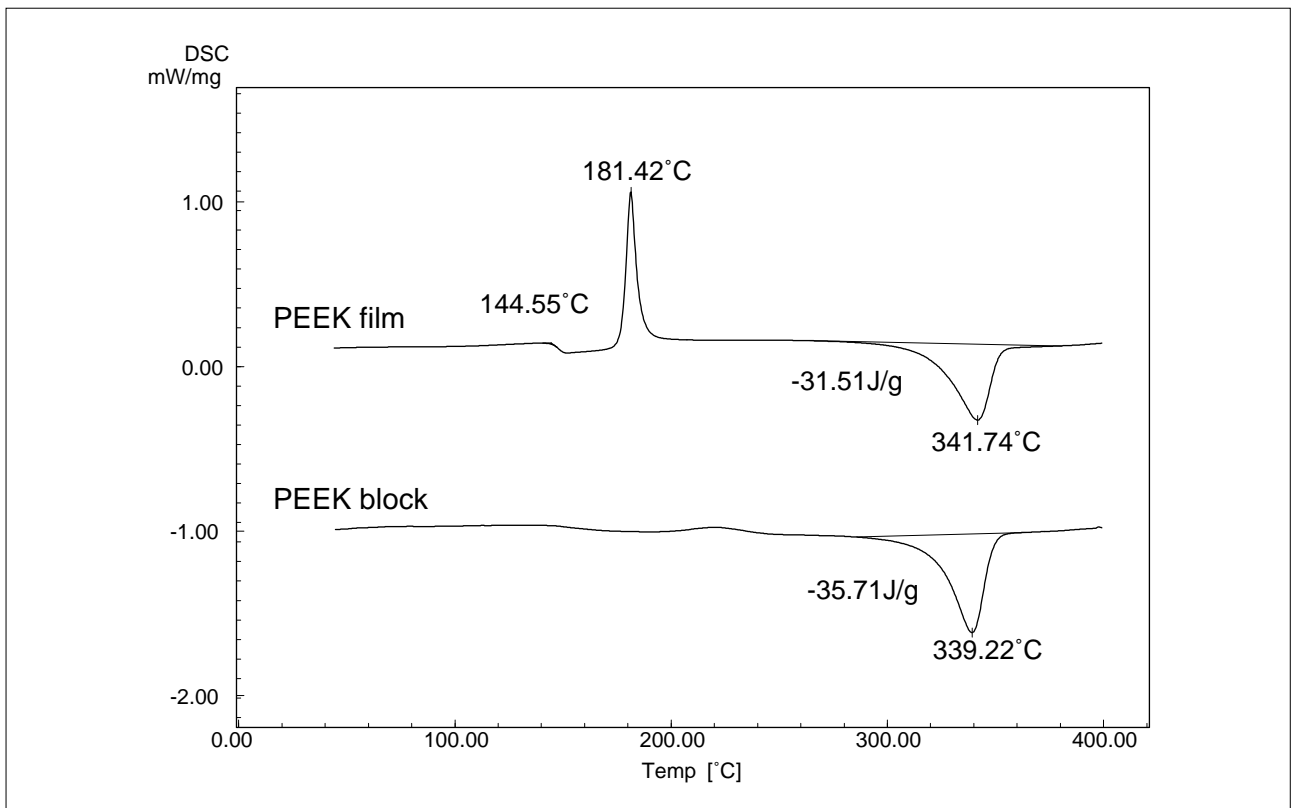


Fig. 1.2.1 DSC curves of PEEK



# 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<sub>2</sub>  
Flow Rate : 40mL/min  
[Temperature Program]  
Heating Rate : 10°C/min  
Cooling Rate : -10°C/min

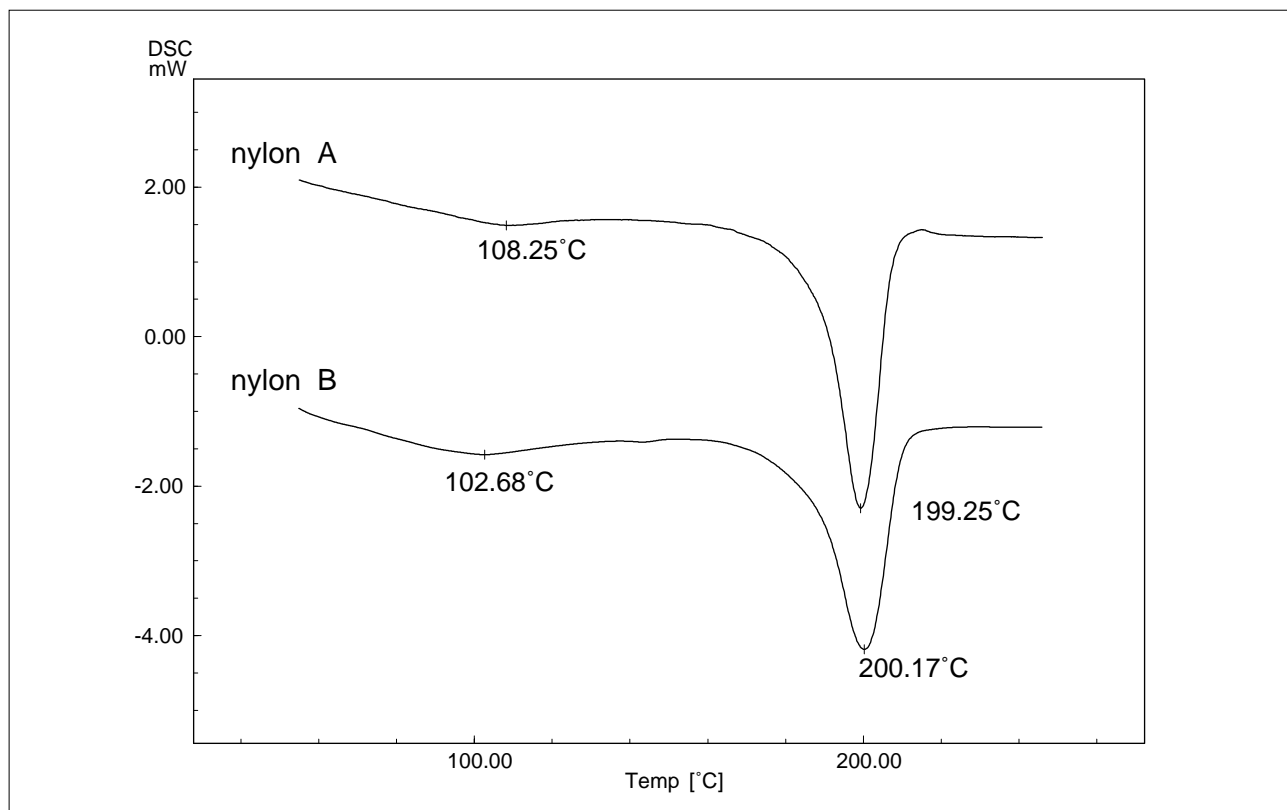


Fig. 2.1.1 DSC curves of nylon A, B (melting)

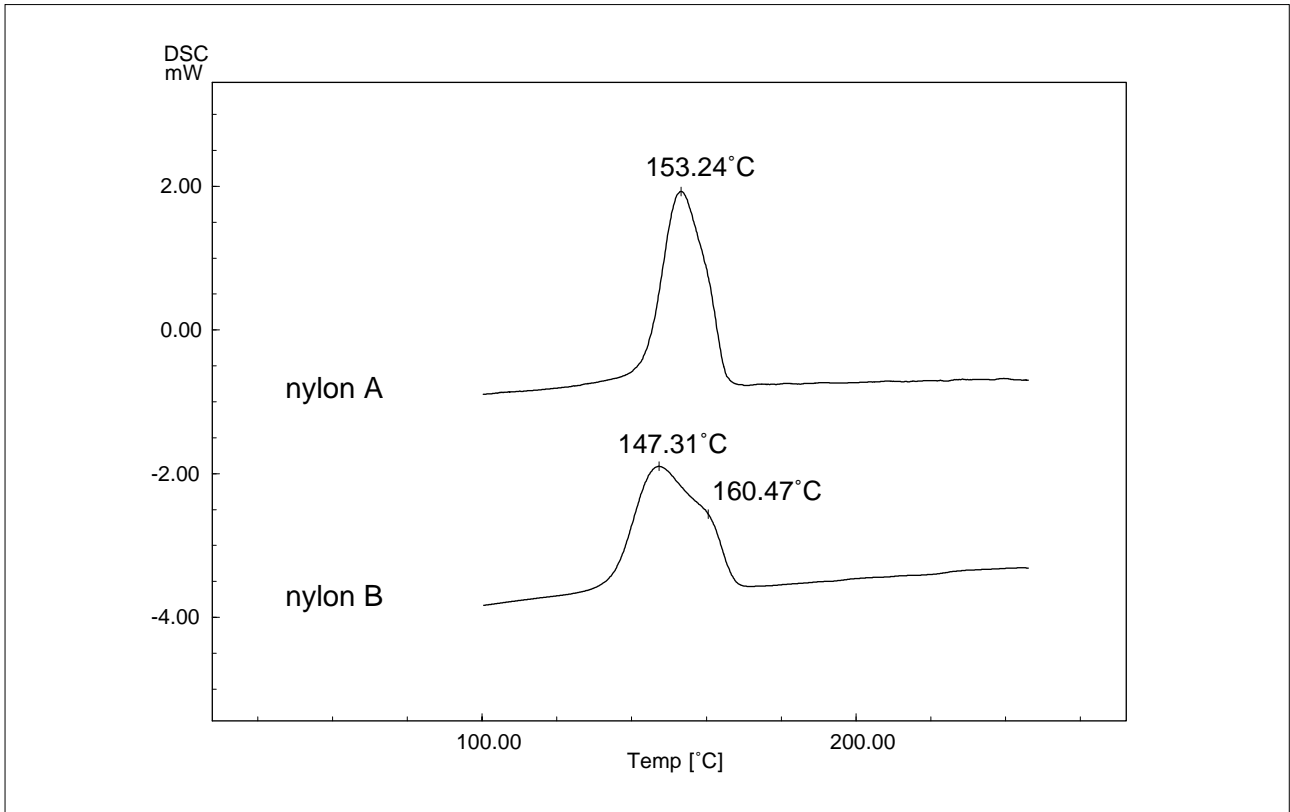


Fig. 2.1.2 DSC curves of nylon A, B (crystallization)



# 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

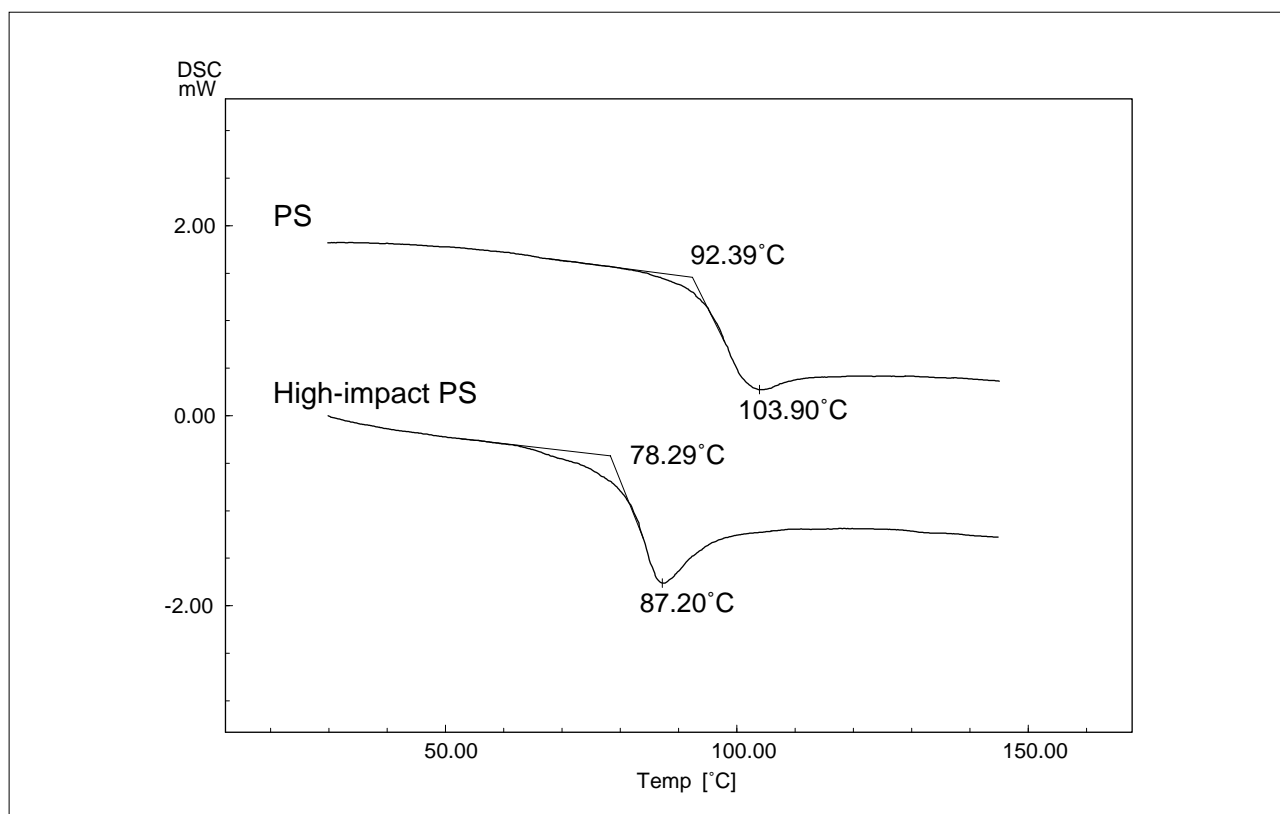


Fig. 3.1.1 DSC curves of PS and High-impact PS

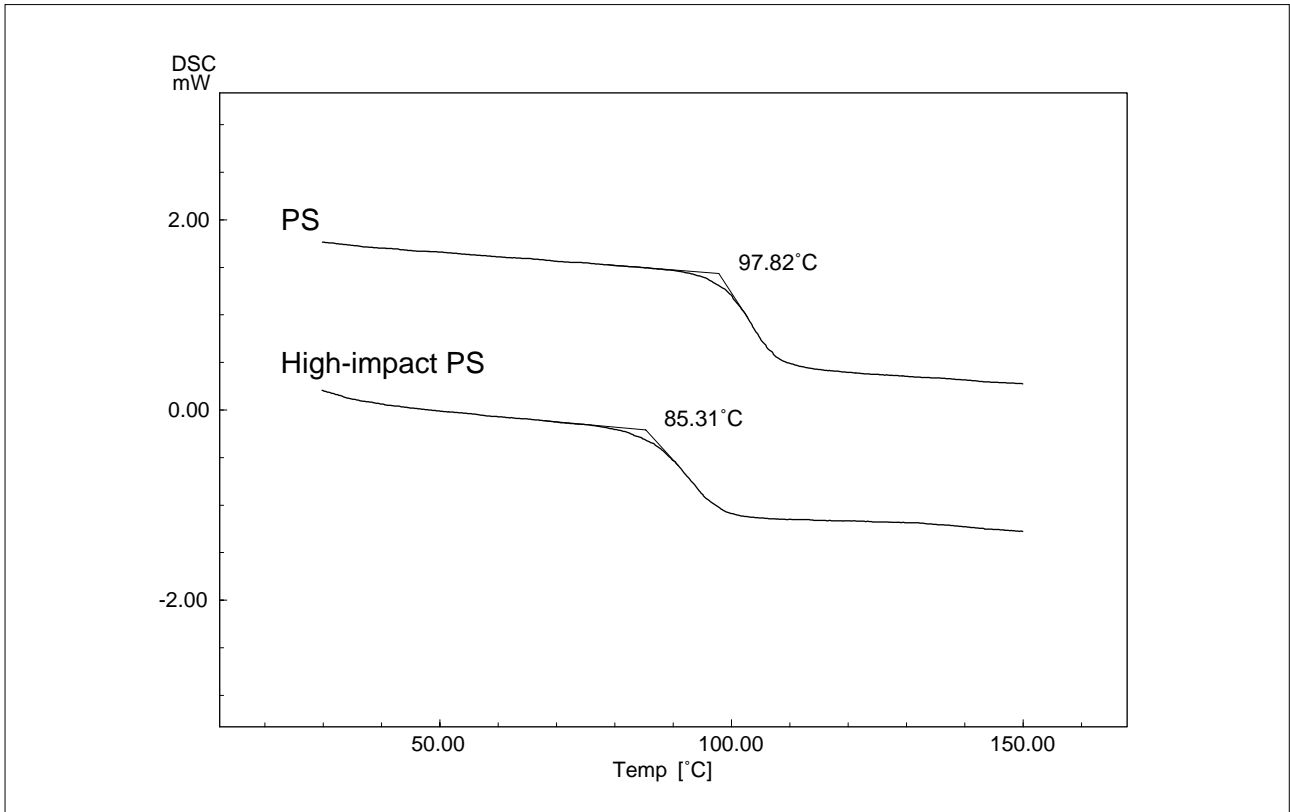


Fig. 3.1.2 DSC curves after heat treatment



## 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

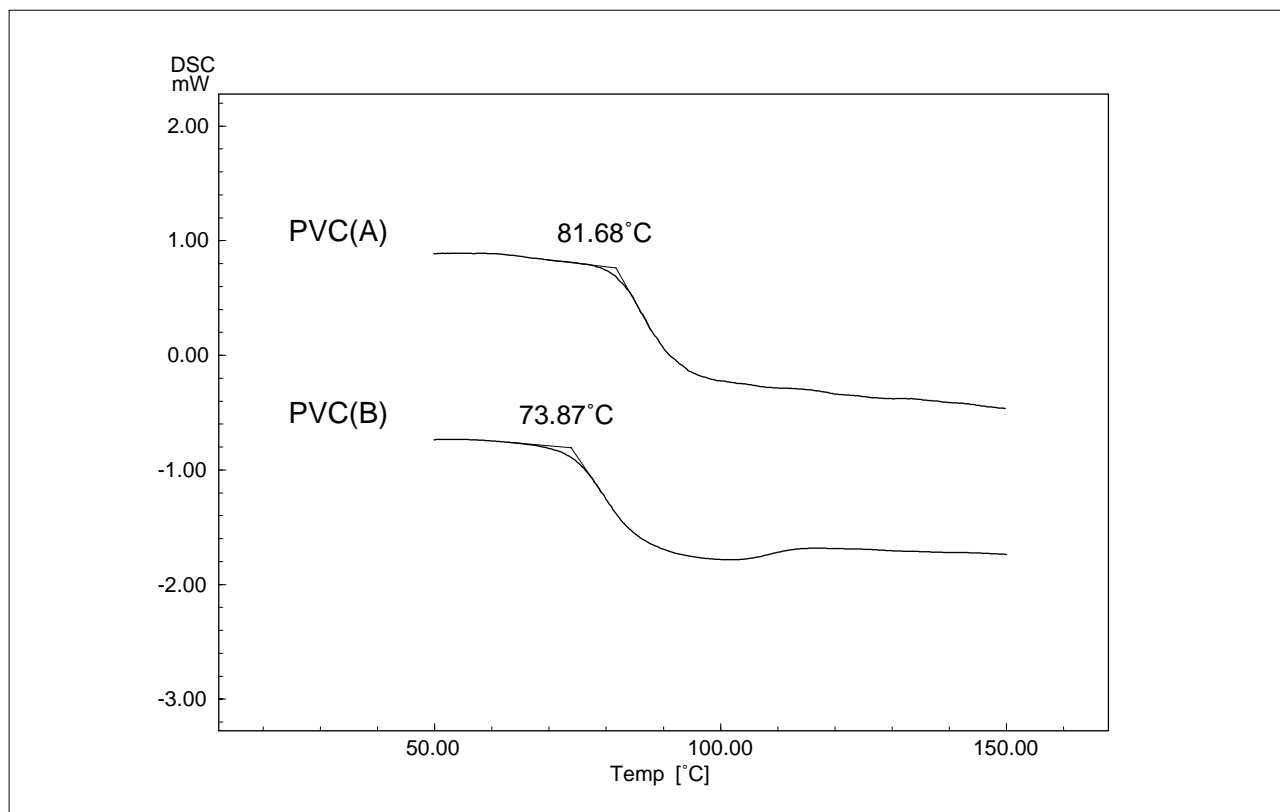


Fig. 3.2.1 DSC curves of PVC

### 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<sub>2</sub>  
Flow Rate : 30mL/min  
[Temperature Program]  
Heating Rate : 20°C/min

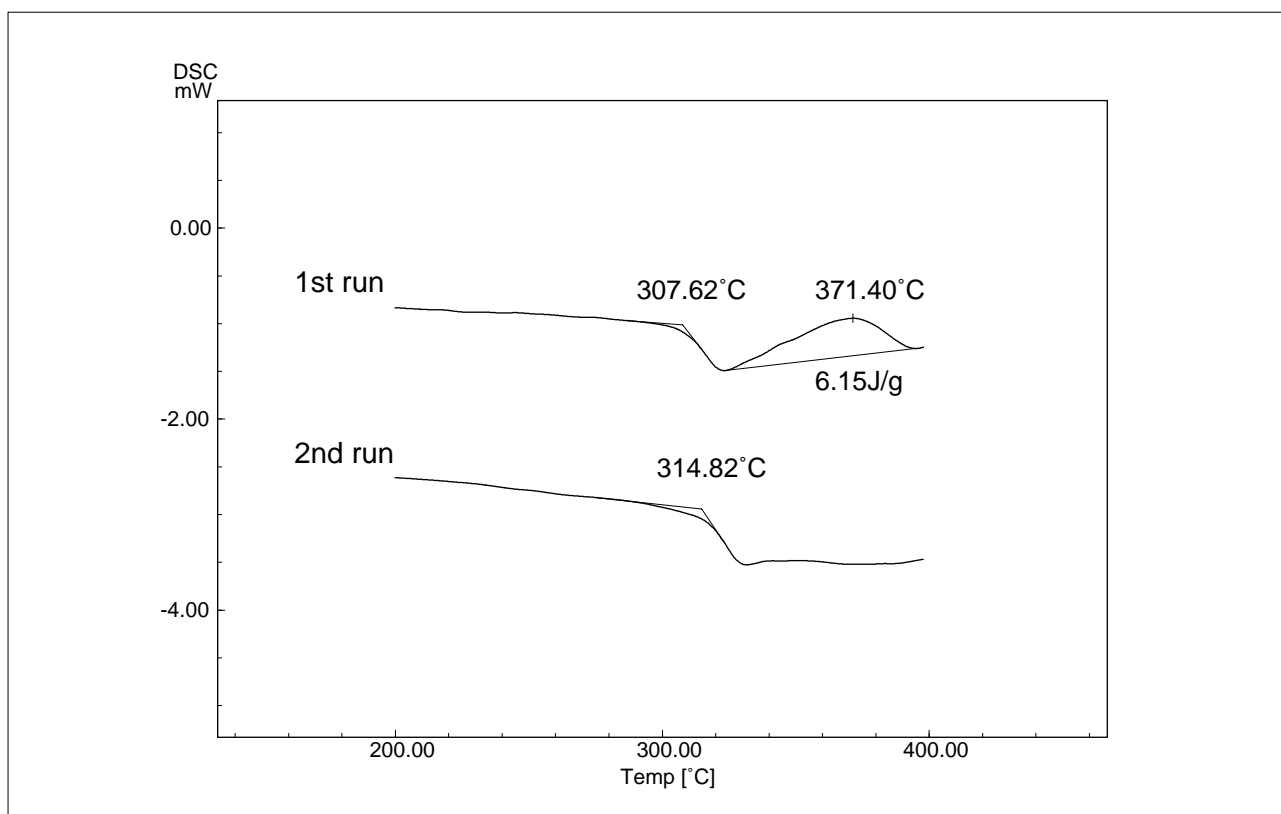


Fig. 3.3.1 DSC curves of Polyimide



# Measurement of Water Content by TG

## 4.1 Water content in polyethyleneterephthalate (PET)

### ■ Explanation

Water content in polymer needs evaluation and control, since it affects the characteristic of polymer.

Here, the trace water of 18 $\mu$ g in PET was quantified.

### ■ Analytical Conditions

Instrument : TGA-50

Sample : PET film

Sample Amount : 31.11mg

[Temperature Program]

Heating Rate : 5°C/min

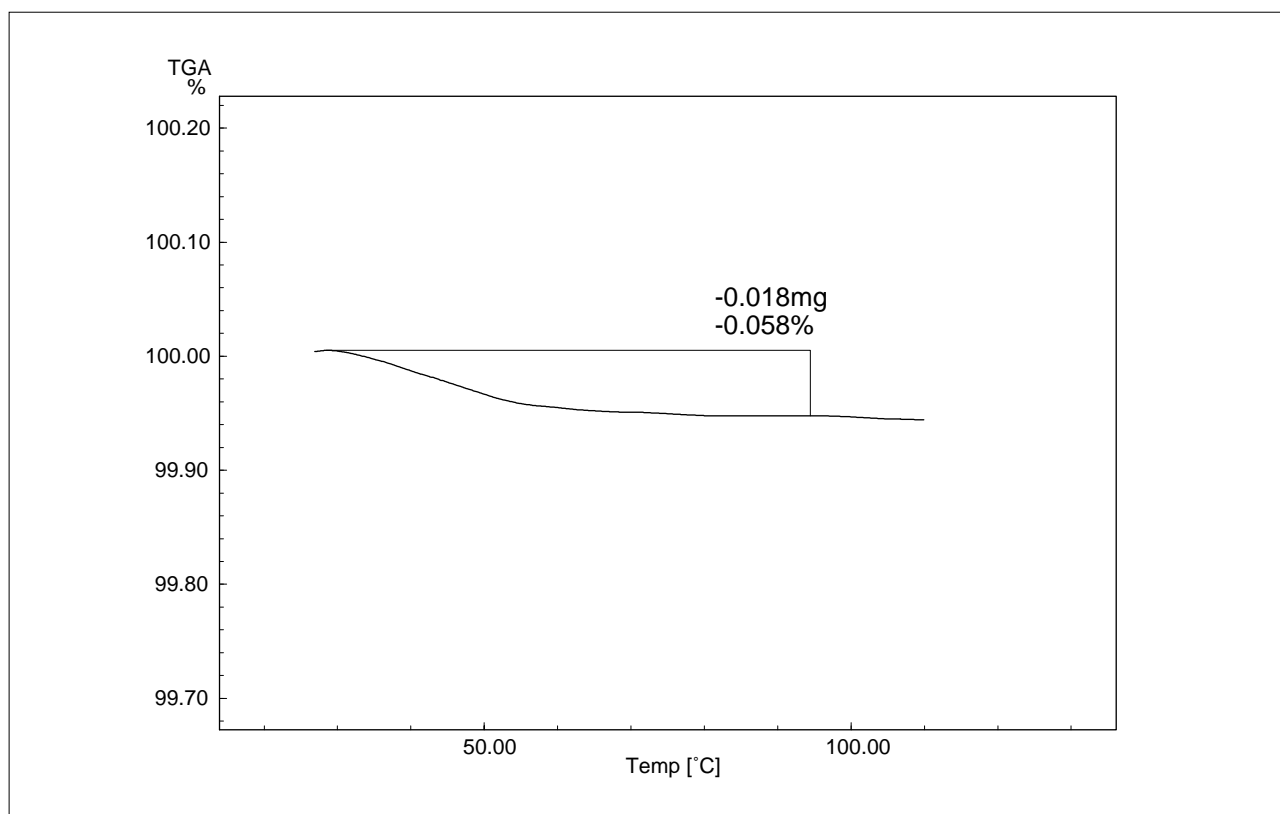


Fig. 4.1.1 TG curve of PET

## 4.2 Water content in polyethyleneterephthalate (PET) fiber

### ■ Explanation

Water content and the trace quantity of volatile components in PET fiber were quantified

Since this sample is a fiber-like, it is difficult to sample in the usual crucible cell ( $\phi 6 \times 5$ mm). It can sample easily by using the large capacity cell of TGA-51 exclusive use, and TG macro crucible ( $\phi 11 \times 14$ mm) (referring to the following figure) this time, and a very small quantity of water of 0.167% and very small quantities of volatile components were measured.

### ■ Analytical Conditions

Instrument : TGA-51  
Sample : PET fiber  
Sample Amount : 422.31mg  
Atmospheric Gas : N<sub>2</sub>  
Flow Rate : 20mL/min  
[Temperature Program]  
Heating Rate : 5°C/min

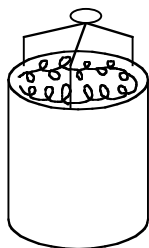


Fig. 4.2.1 Macro crucible

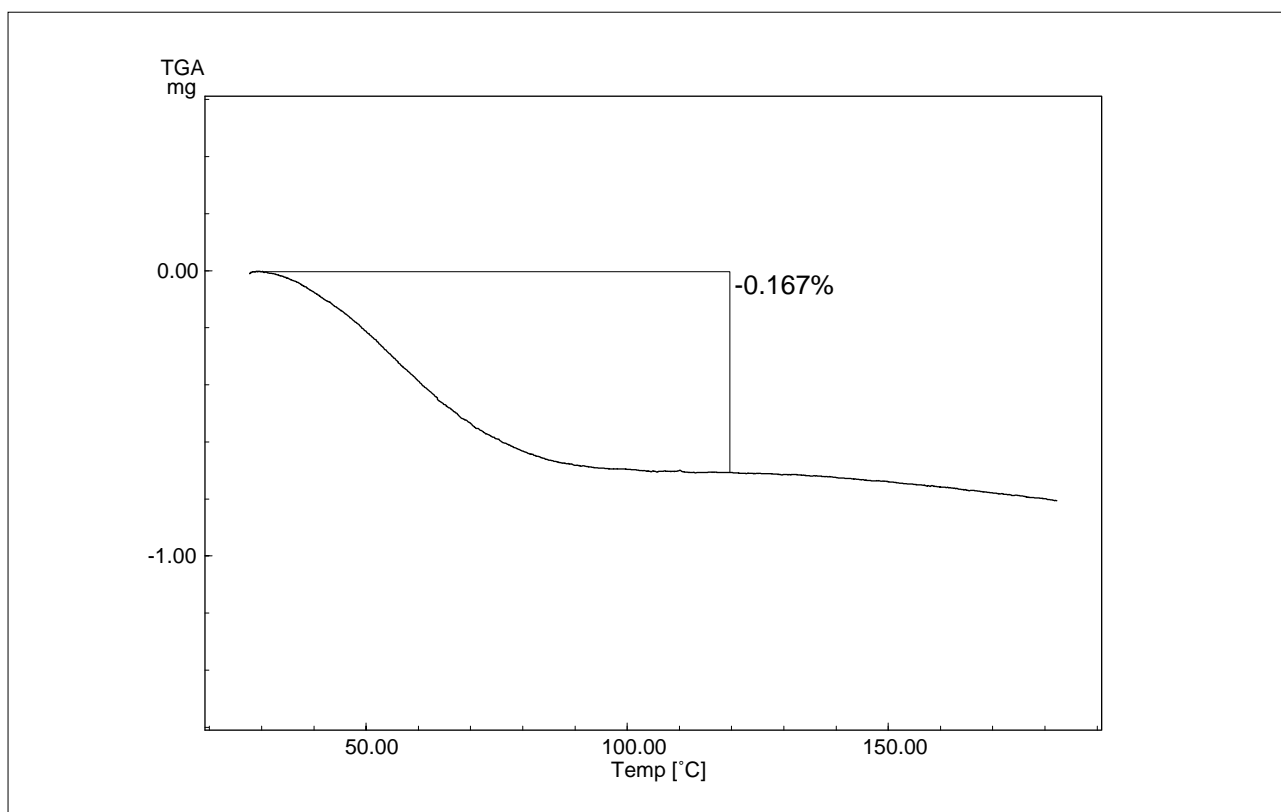


Fig. 4.2.2 TG curve of PET fiber

### 4.3 Water content in polyimide (PI) film

#### ■ Explanation

Since this PI is a film-like, a sampling was difficult in the usual cell, as shown in the following figure, PI film was squarely cut in accordance with the height of TG macro crucible

( $\phi 10 \times 12$ mm) and the rounded film was put in the crucible.

Since the measuring was carried out using a large amount of sample of 300mg, a very slight loss in quantity of 1.145% could be detected with high sensitivity.

#### ■ Analytical Conditions

Instrument : TGA-51  
Sample : PI film  
Sample Amount : 311.12mg  
Atmospheric Gas : N<sub>2</sub>  
Cell : Platinum crucible  
Flow Rate : 20mL/min  
[Temperature Program]  
Heating Rate : 10°C/min

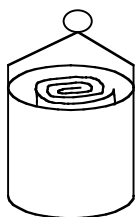


Fig. 4.3.1 Sampling of a film-like sample

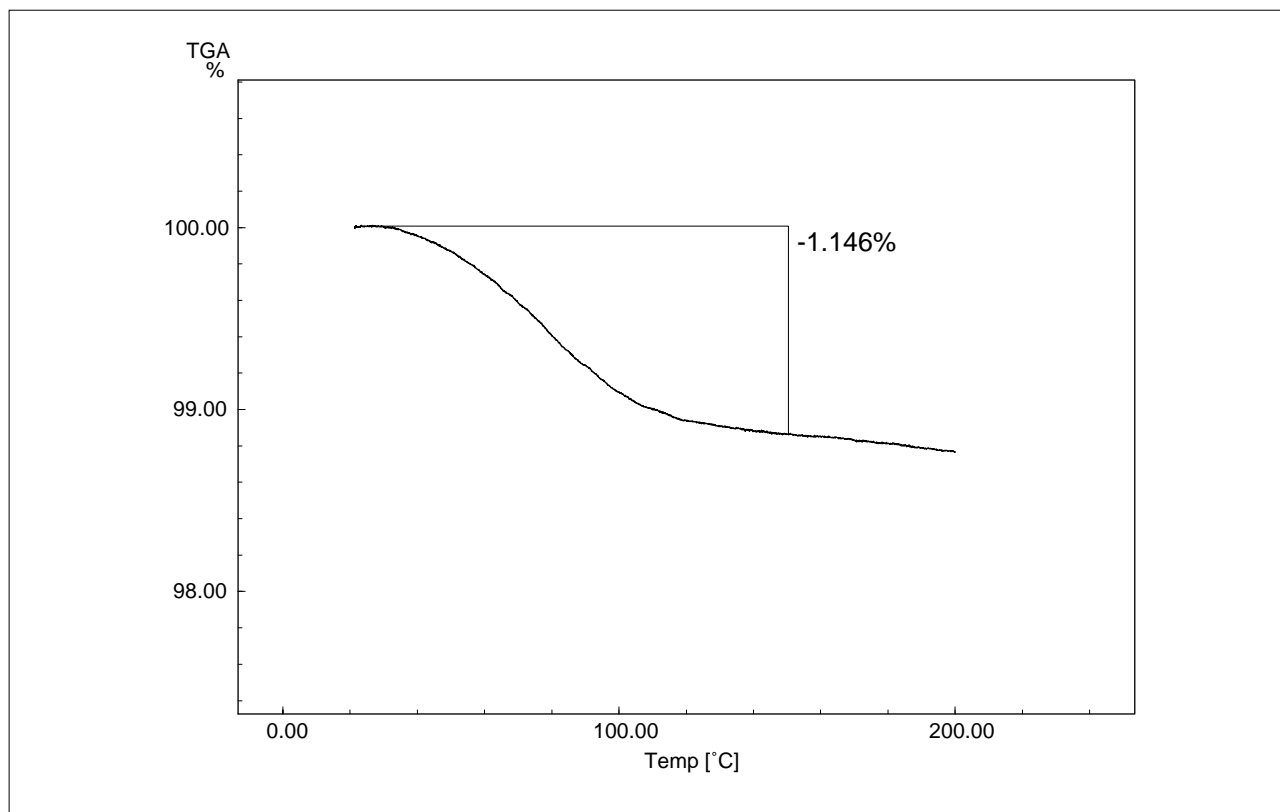


Fig. 4.3.2 TG curve of PI film



# Measurement of Decomposition and Oxidation Reaction

## 5.1 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 decomposition 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<sub>2</sub>  
[Temperature Program]  
Heating Rate : 10°C/min

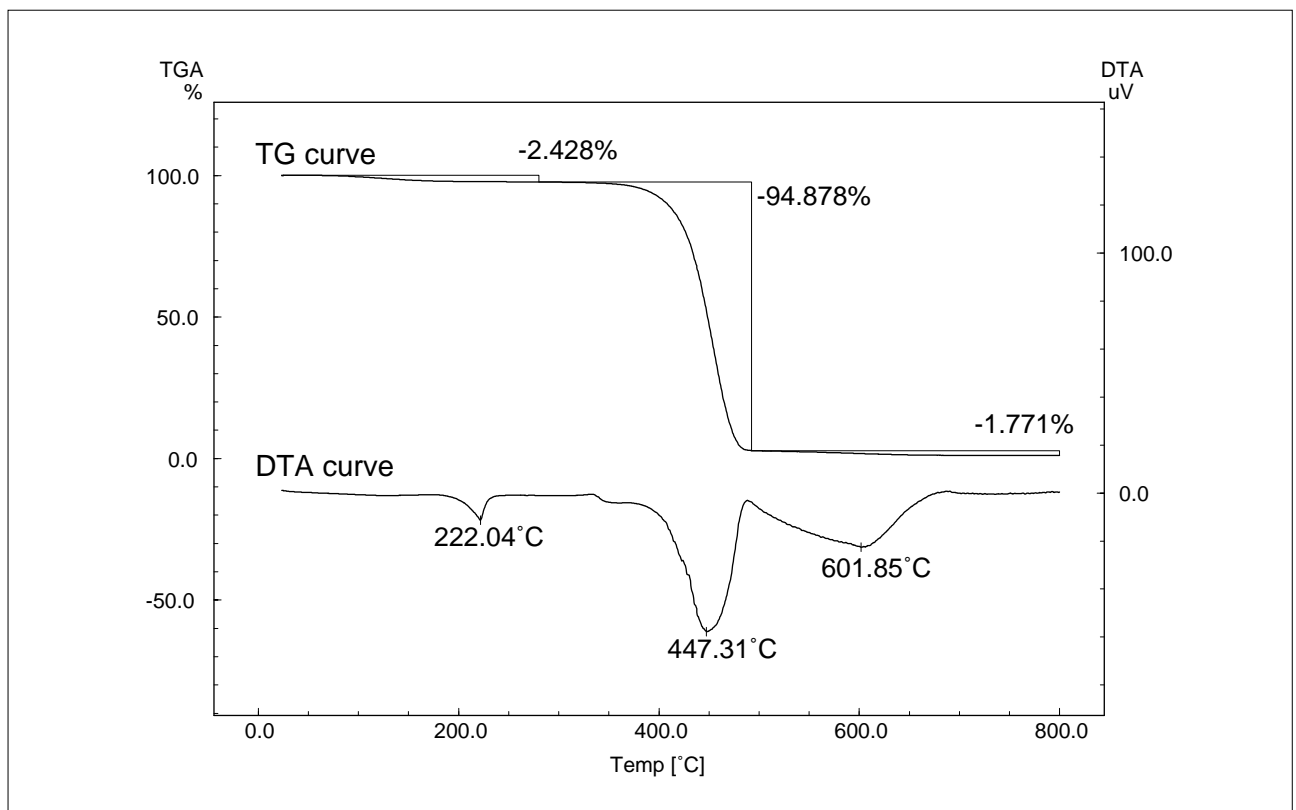


Fig. 5.1.1 TG-DTA curves of nylon 6



## 5.2 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.5.2.1)	: modified PPO
Sample Amount(Fig.5.2.1)	: 12.05mg
Sample(Fig.5.2.2)	: modified PPO
Sample Amount(Fig.5.2.2)	: 11.6mg
Atmospheric Gas	: N <sub>2</sub>
Flow Rate	: 30mL/min
[Temperature Program]	
Heating Rate(Fig.5.2.1)	: 10°C/min
Holding Temperature(Fig.5.2.2)	: 300°C

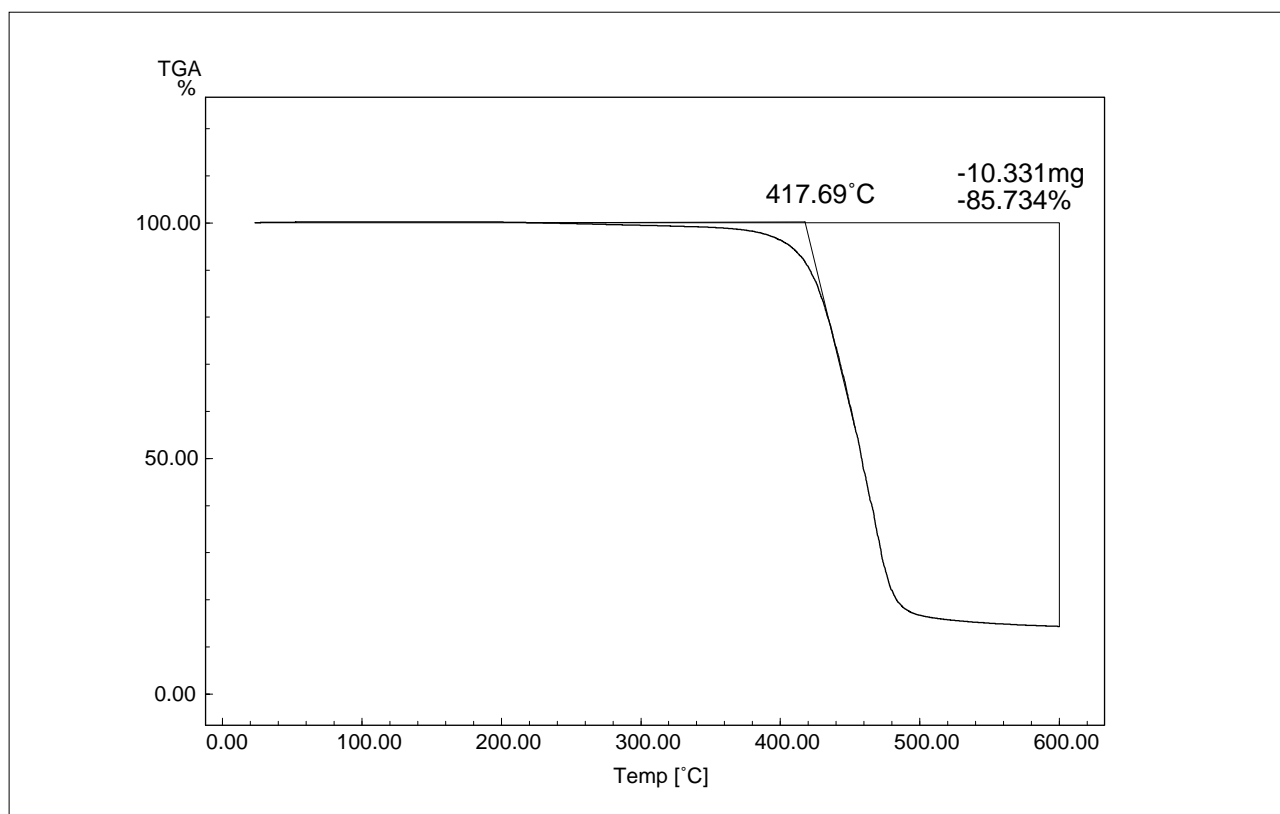


Fig. 5.2.1 TG curve of modified PPO

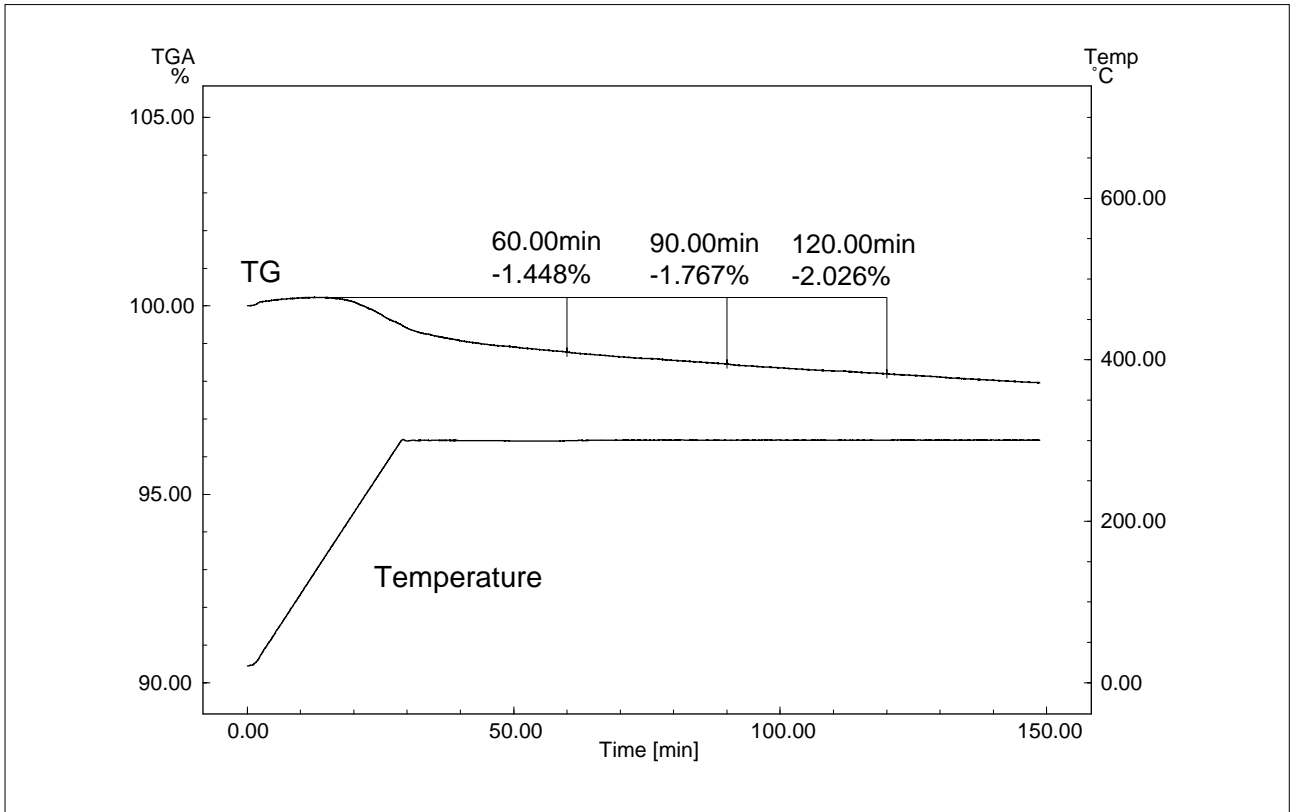


Fig. 5.2.2 TG curve of modified PPO (Isothermal)



## 5.3 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.5.3.1) : PET

Sample Amount(Fig.5.3.1) : 10.71mg

Sample(Fig.5.3.2) : PET

Sample Amount(Fig.5.3.2) : 11.32mg

Atmospheric Gas : N<sub>2</sub>

Flow Rate : 30mL/min

[Temperature Program]

Heating Rate(Fig.5.3.1) : 10°C/min

Holding Temperature(Fig.5.3.2) : 280°C

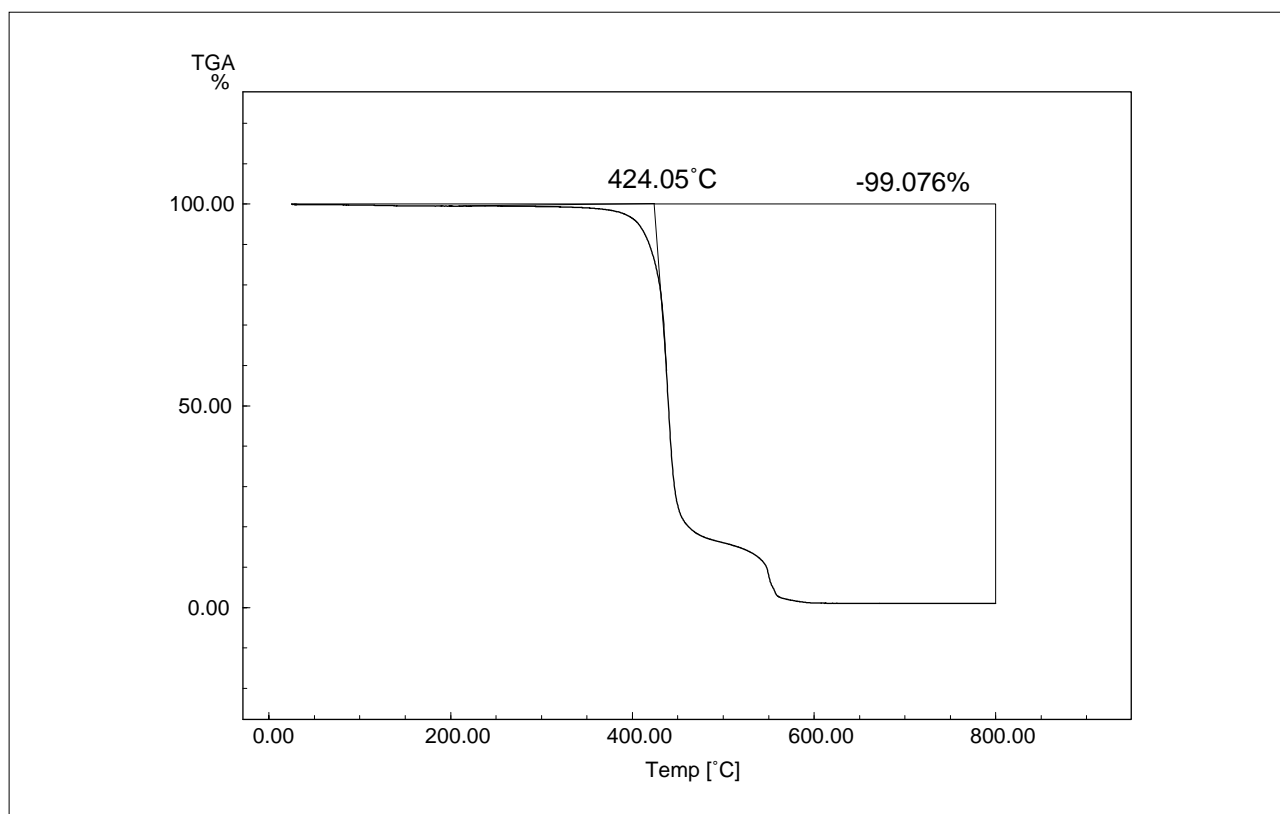


Fig. 5.3.1 Programmed Thermal Decomposition of PET

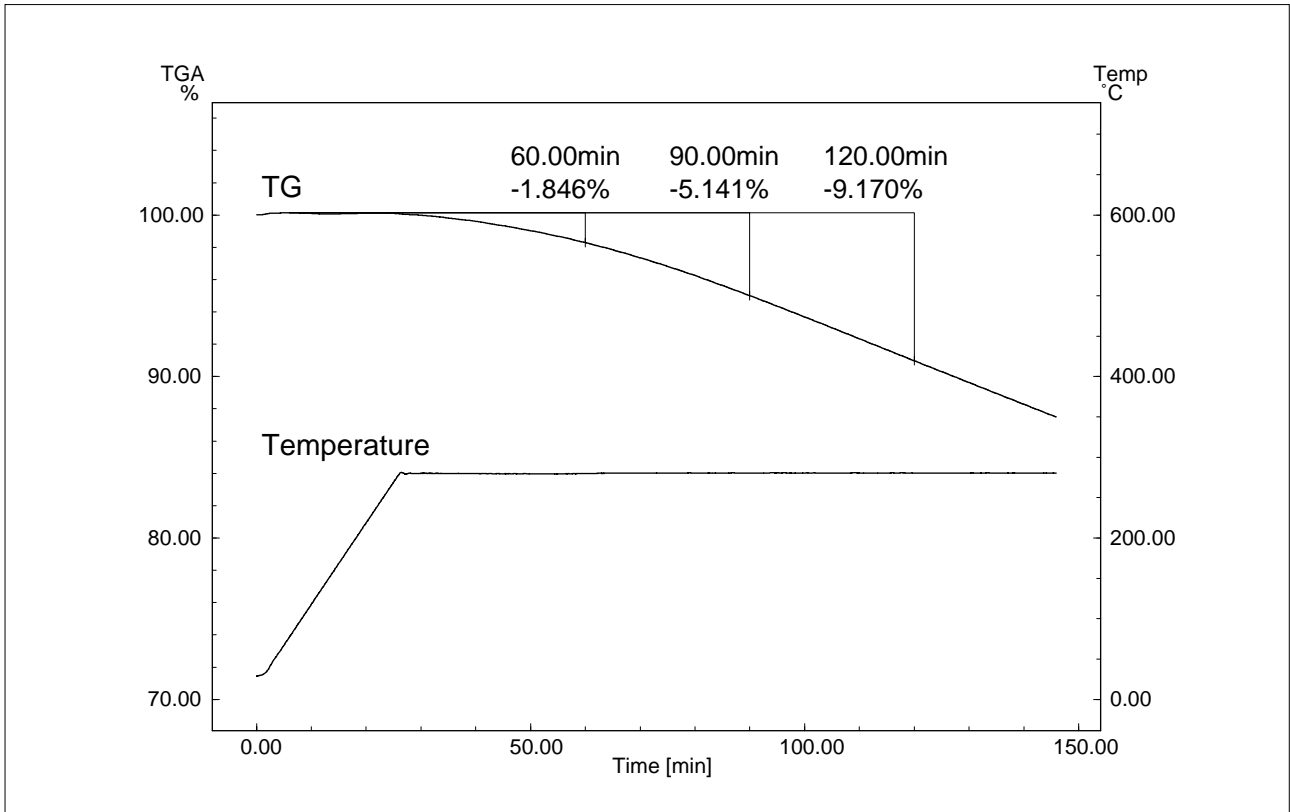


Fig. 5.3.2 Isothermal Decomposition of PET

## 5.4 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.5.4.1) : 5.05mg

Sample Amount(Fig.5.4.2) : 5.05mg

Atmospheric Gas : N<sub>2</sub>→O<sub>2</sub>

Flow Rate : 50mL/min

[Temperature Program]

Holding Temperature(Fig.5.4.1) : 190°C

Holding Temperature(Fig.5.4.2) : 200°C

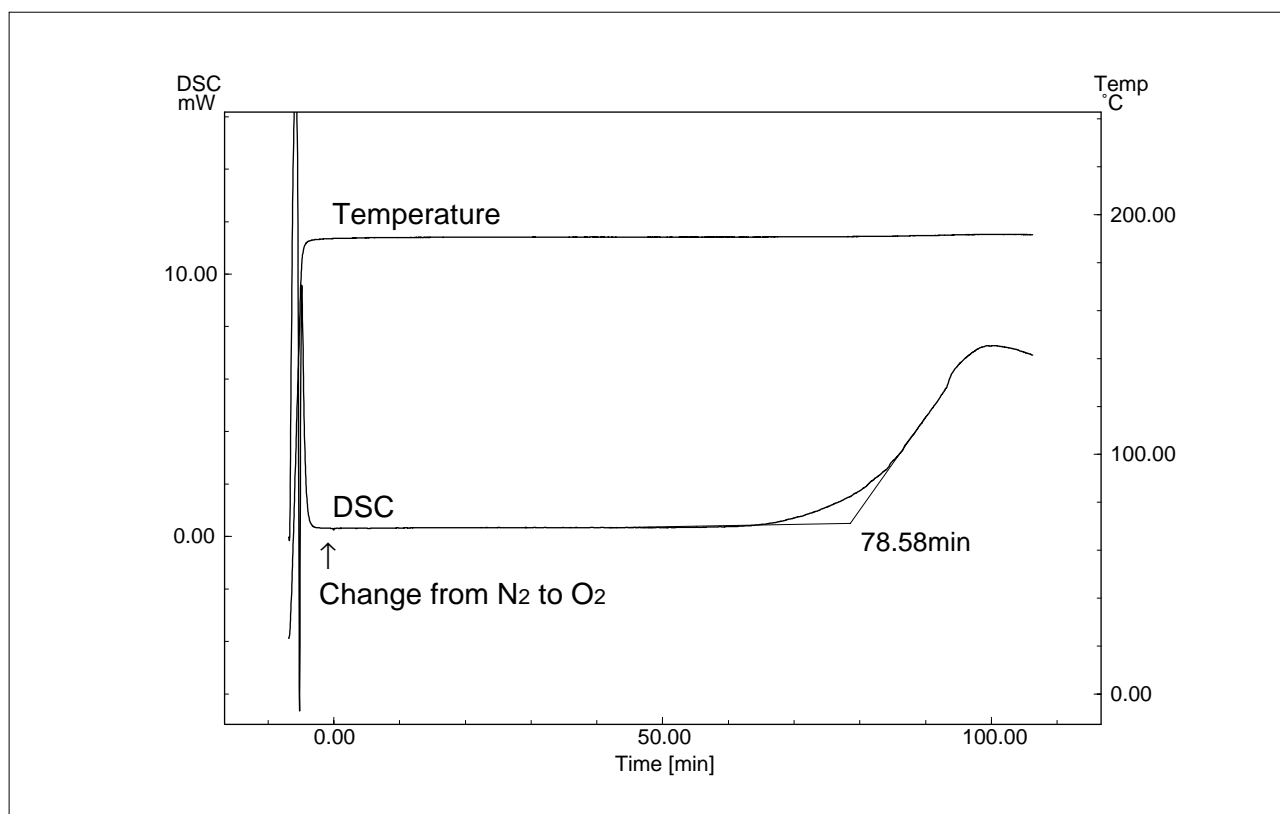


Fig. 5.4.1 Oxygen induction time of PE at 190°C

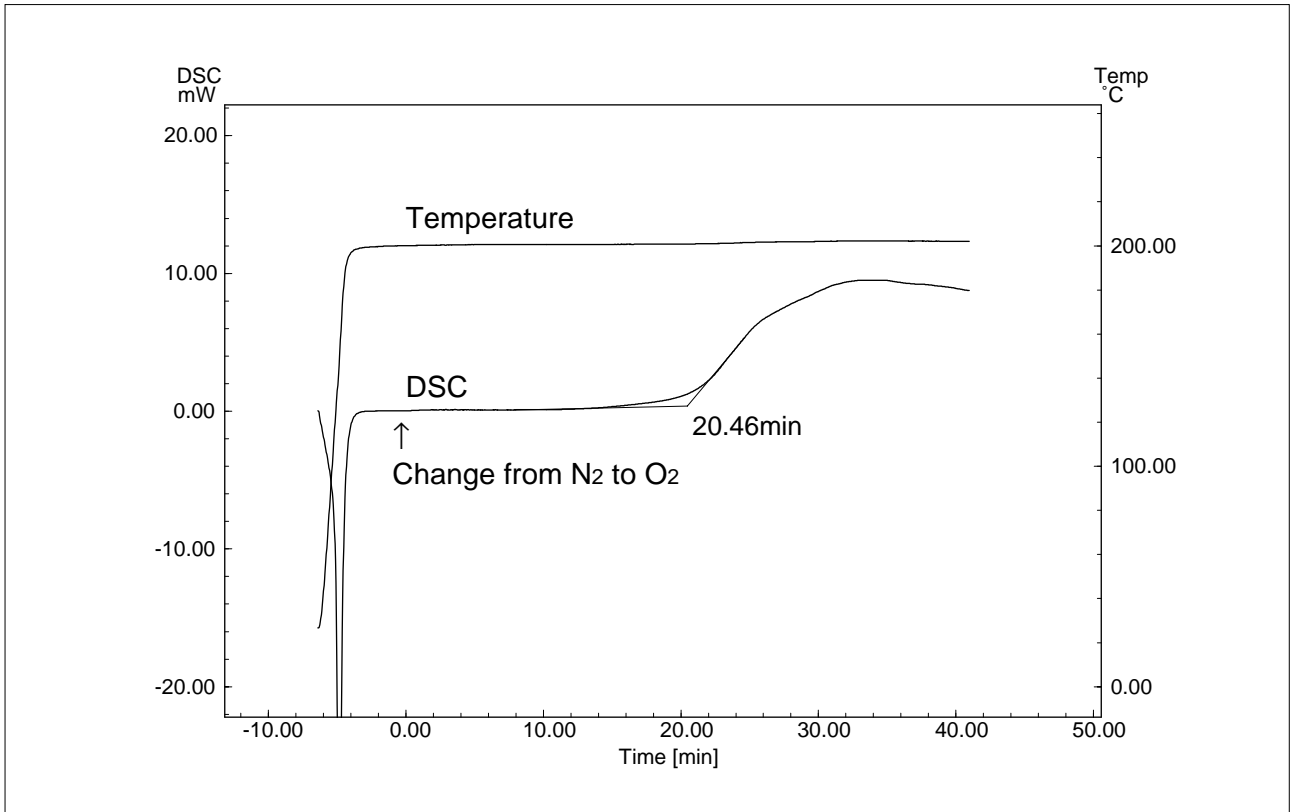


Fig. 5.4.2 Oxygen induction time of PE at 200°C



## 5.5. Thermal decomposition of Teflon

### ■ Explanation

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

### ■ Analytical Conditions

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

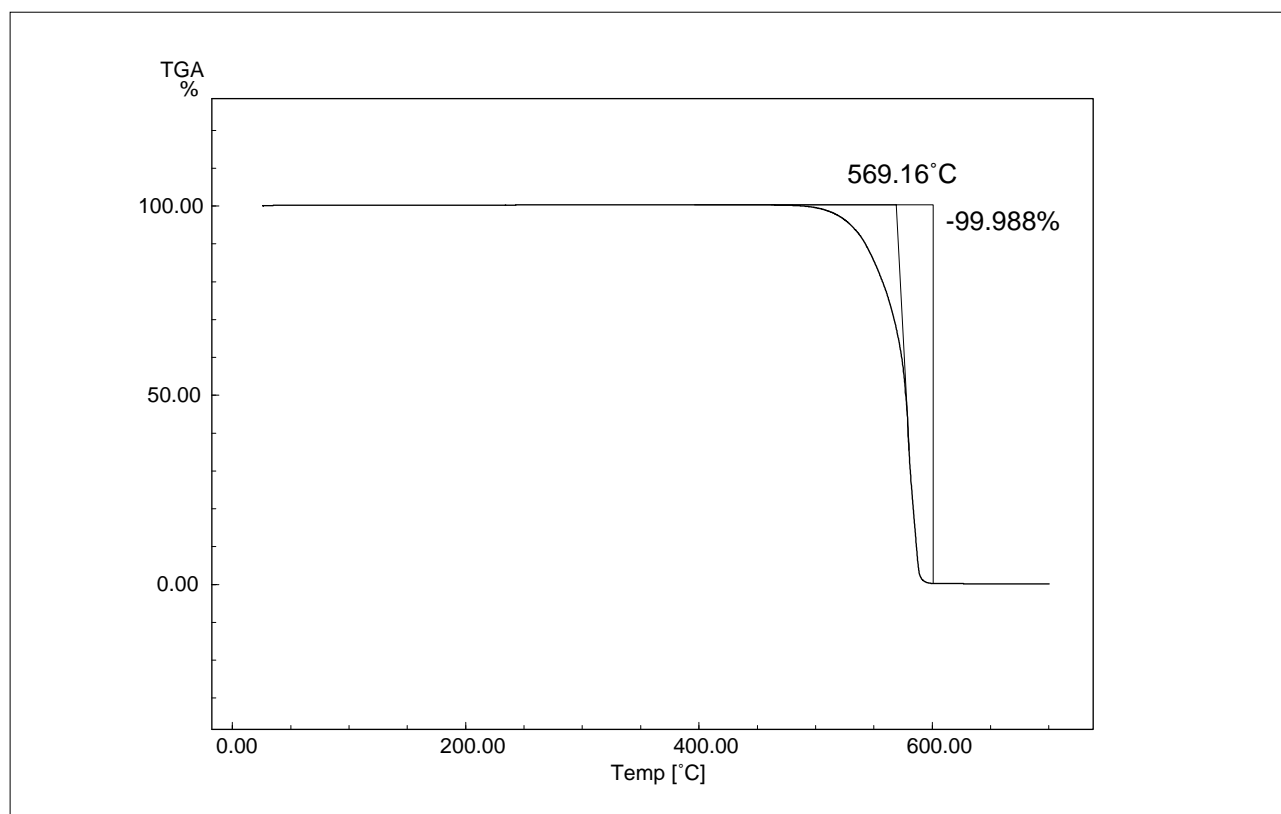


Fig. 5.5.1 TG curve of Teflon



# Condensation Reaction of Phenol Resin ■

## 6.1 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<sub>2</sub>  
Flow Rate : 30mL/min  
[Temperature Program]  
Heating Rate : 10°C/min

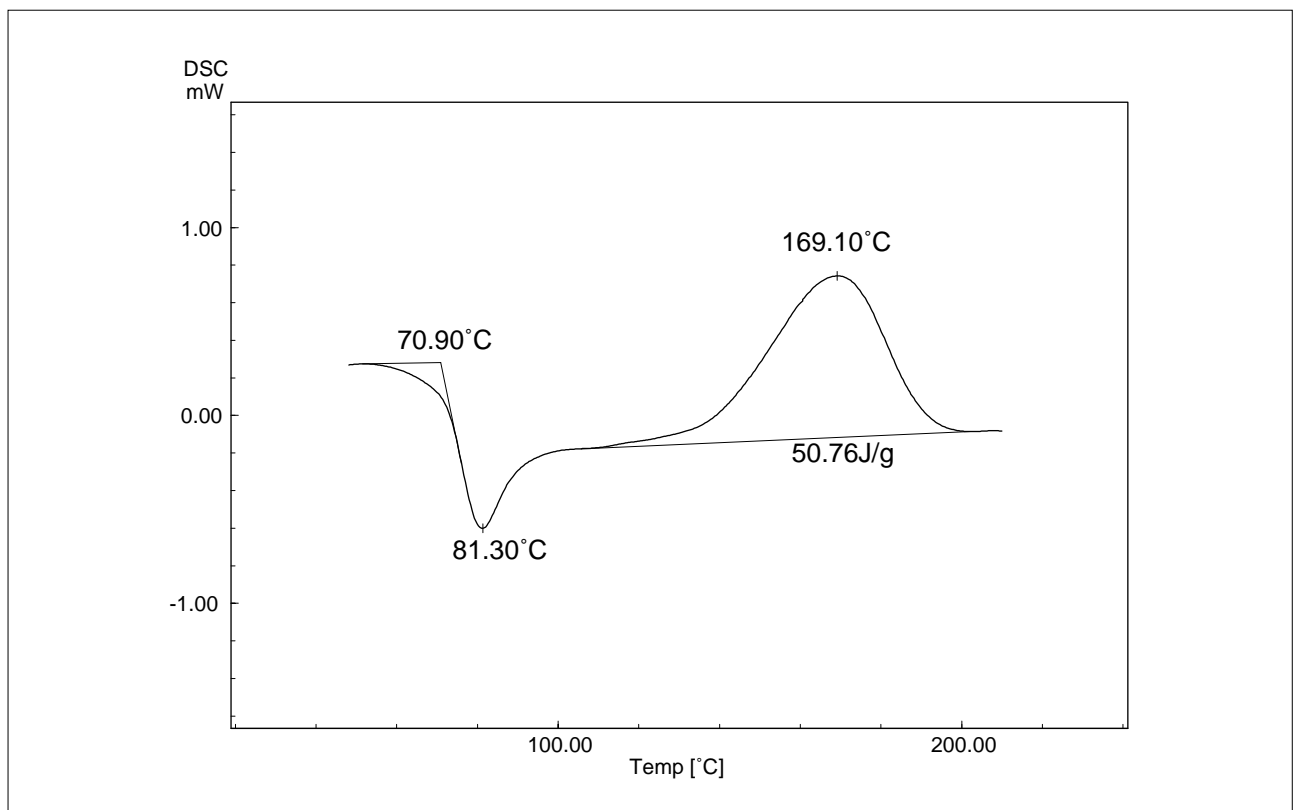


Fig. 6.1.1 DSC curve of Phenol Resin



# Quantification of Reinforcing Materials

## 7.1 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

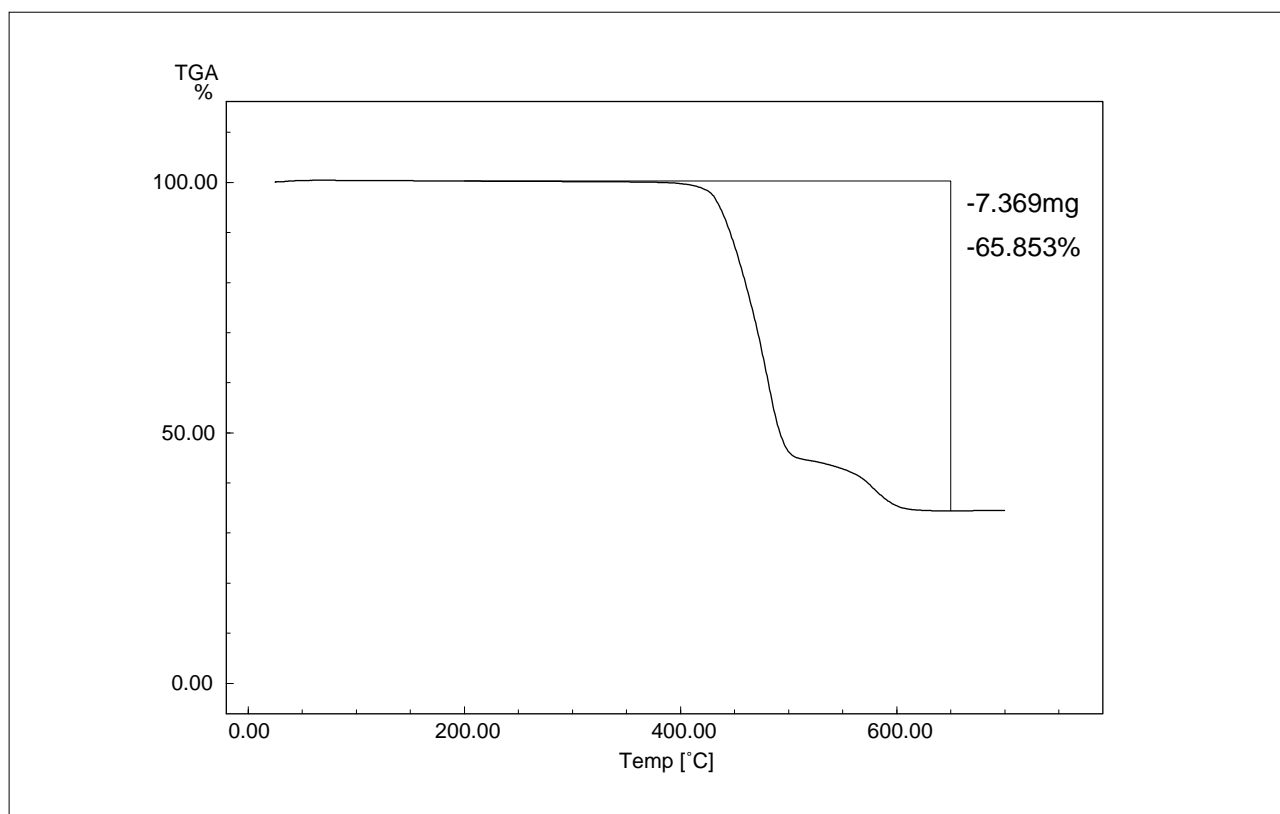


Fig. 7.1.1 TG curve of PET

## 7.2 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<sub>2</sub>→Air  
[Temperature Program]  
Heating Rate : 20°C/min

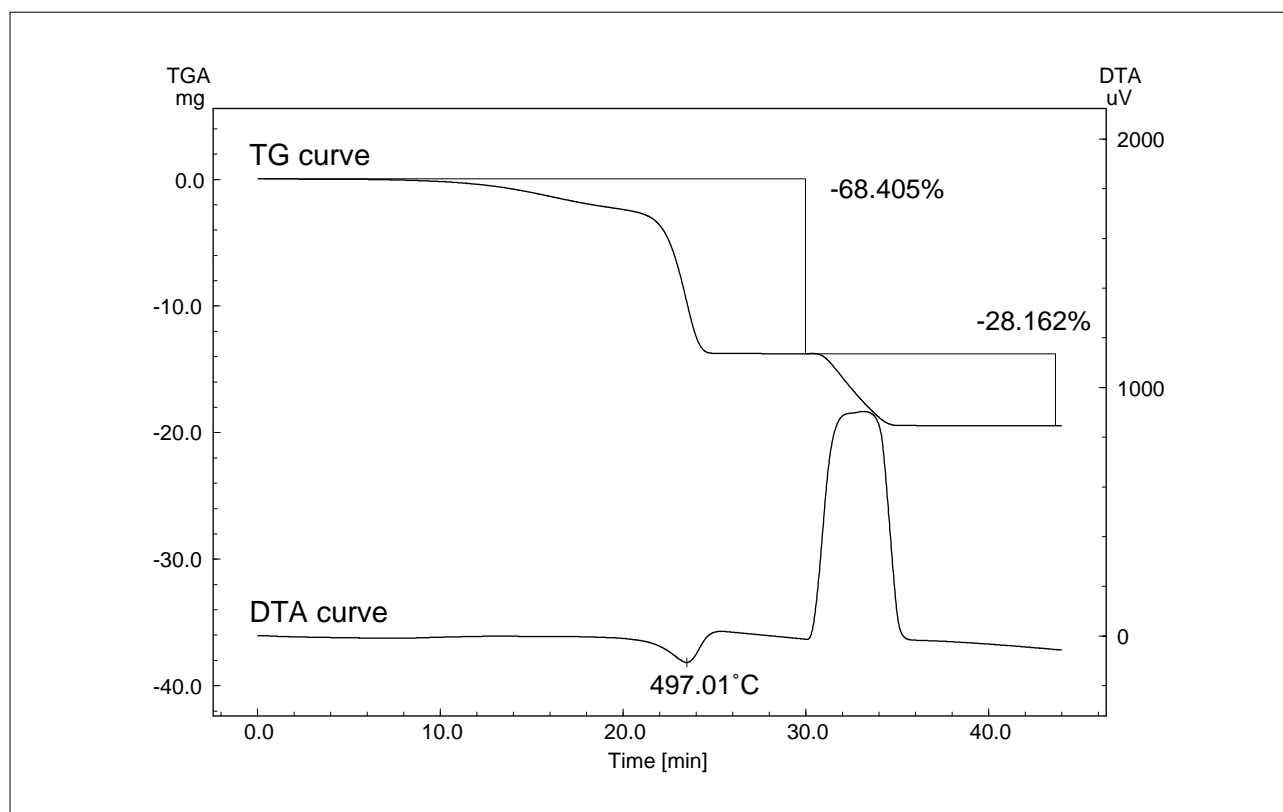


Fig. 7.2.1 TG-DTA curves of SBR



# TMA Measurement

## 8.1 Thermal stress of polyethyleneterephthalate (PET) fiber

### ■ Explanation

Thermal stress measurement is the method which measures the strength of stress to the change of temperature after giving a constant strain to a sample and maintaining the rate of strain, and can know size stability, form stability, etc. Here, PET fiber was measured. 1% of strain was given to the sample and heated. The increase in stress is observed from 97.6°C. This was caused by the shrinkage of strained fiber. In case of the sample that was made by being strained and oriented, if it exceeds the processing temperature at the time of drawing, the orientation is canceled and the shrinkage is observed. After that, the stress decreases gradually, and the sample melts near 255°C, then the stress becomes 0.

### ■ Analytical Conditions

Instrument : TMA-60  
Sample : PET fiber  
Sample Length : 15.25mm  
[Temperature Program]  
Heating Rate : 10°C/min

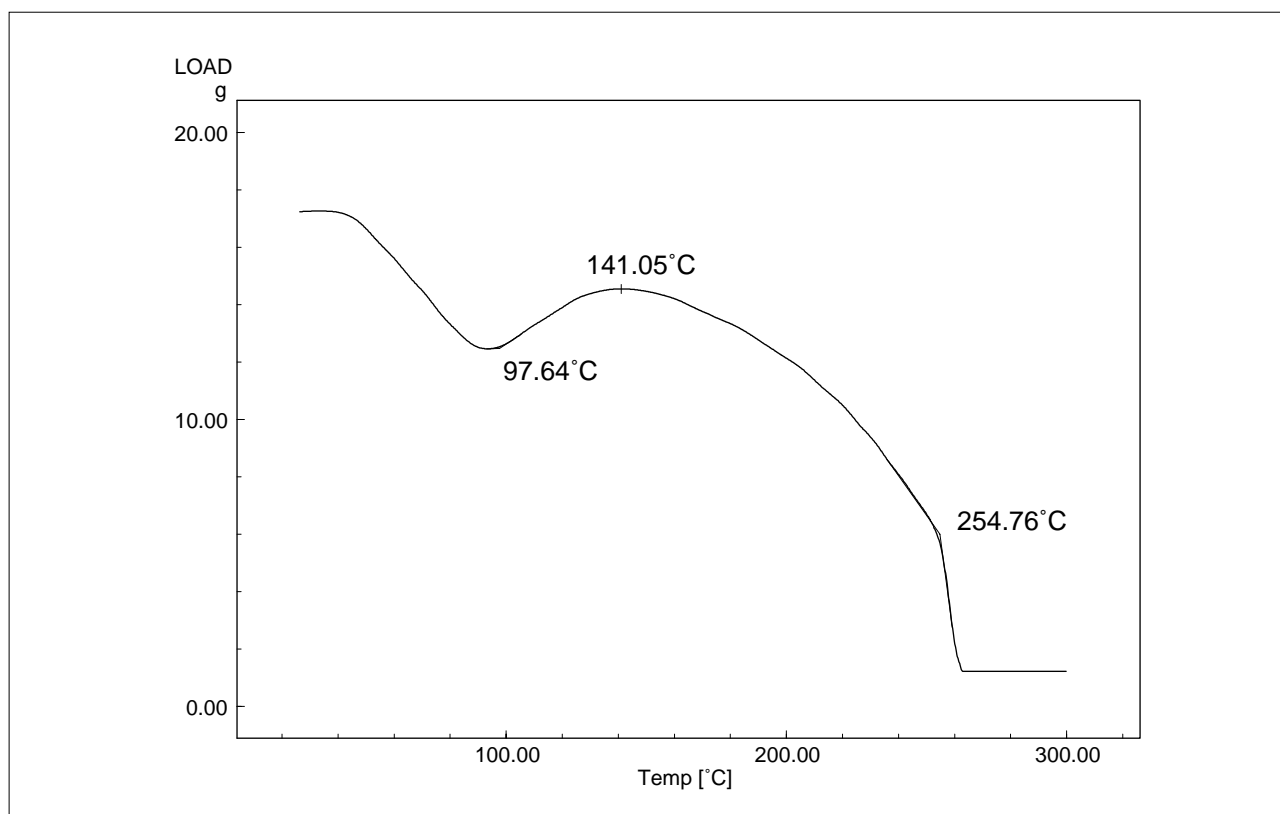


Fig. 8.1.1 Thermal stress measurement of PET fiber

## 8.2 Shrink stress of magnetic tape

### ■ Explanation

Shrink stress measurement is the method that generates power and measures that power so that it may not shrink, when the strain of a sample is set to 0 and a sample shrinks by heating. Here, the magnetic tape was measured.

It turns out that the shrinkage starts from 100.7°C, and the stress became 27.2g at maximum.

### ■ Analytical Conditions

Instrument : TMA-60  
Sample : Magnetic tape  
Sample Length : 12.25mm  
[Temperature Program]  
Heating Rate : 10°C/min

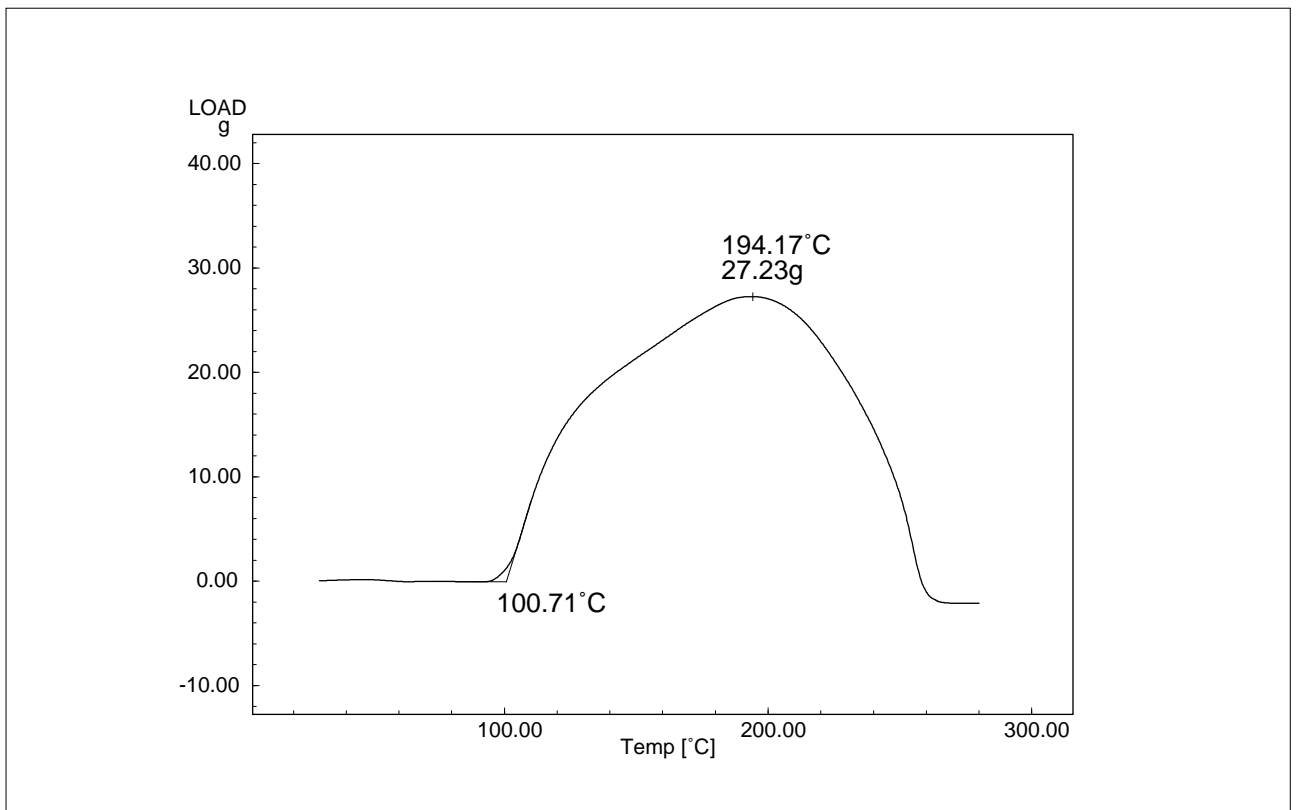


Fig. 8.2.1 Shrink stress measurement of magnetic tape



## 8.3 Softening temperature of polymethylmethacrylate (PMMA)

### ■ Explanation

Penetration measurement can be used as an index that mainly estimates the softening temperature and the heat modification temperature of plastic material.

Here, the softening temperature of PMMA was measured. It turns out that softening of a sample has occurred from near 111.6°C.

### ■ Analytical Conditions

Instrument : TMA-60

Sample : PMMA

Sample Length : 10.03mm

[Temperature Program]

Heating Rate : 5°C/min

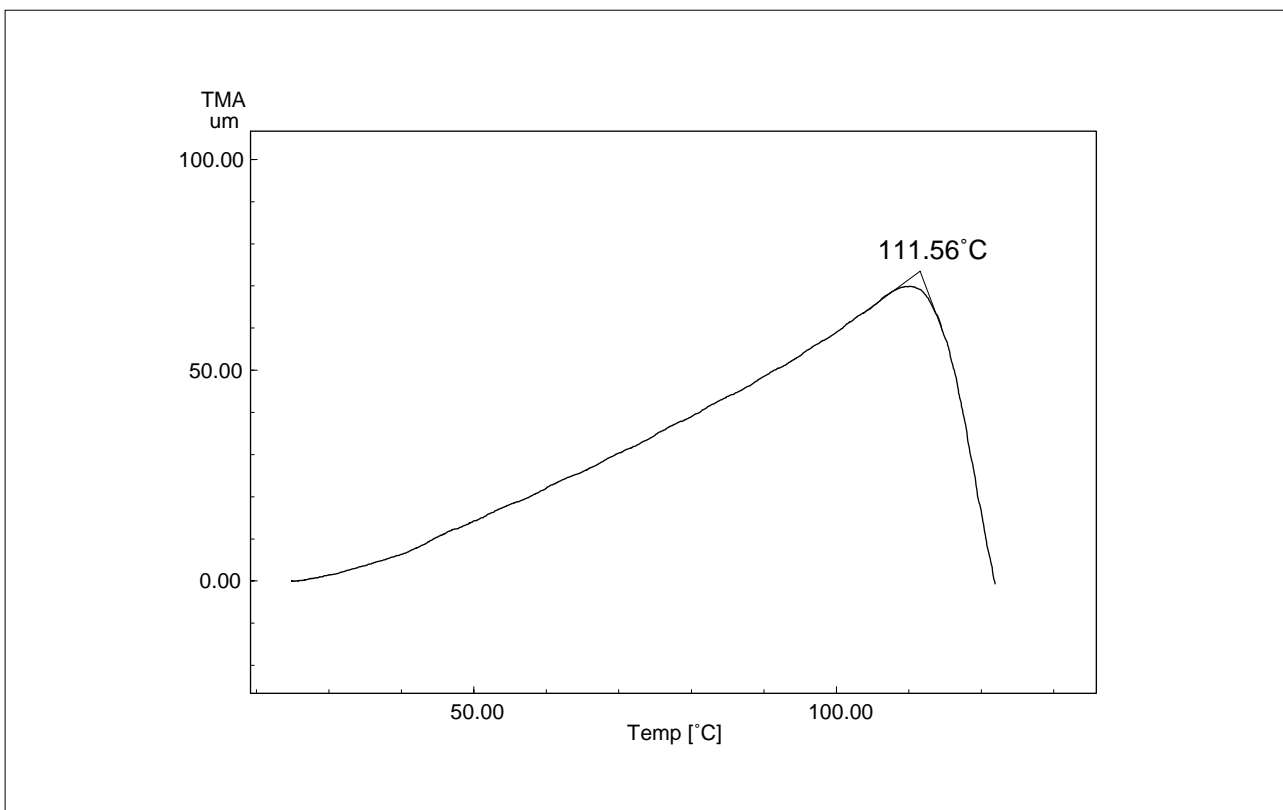


Fig. 8.3.1 TMA curve of PMMA



## 9.1 Thermal expansion of a printed circuit board

### ■ Explanation

With the parts with which an epoxy resin is joined to metal like a printed circuit board or IC, a coefficient of thermal expansion becomes important. Here, the expansion curve of a printed circuit board is shown. The inflection point of glass transition is observed near 90°C, and it turns out that the coefficient of thermal expansion is changing remarkably before and behind it.

### ■ Analytical Conditions

Instrument : TMA-60  
Sample : Printed circuit board  
Sample Length : 10.01mm  
[Temperature Program]  
Heating Rate : 5°C/min

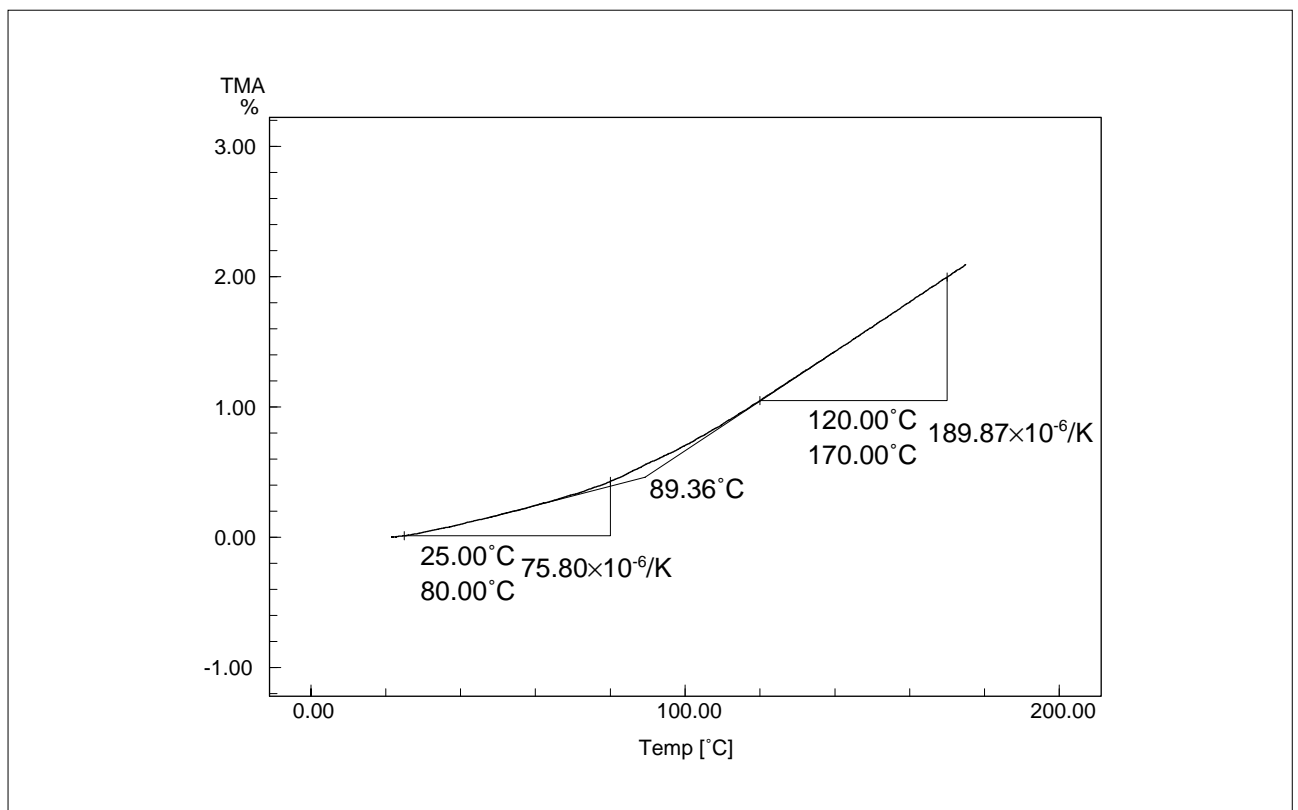


Fig. 9.1.1 TMA curve of a Printed circuit board



## 9.2 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

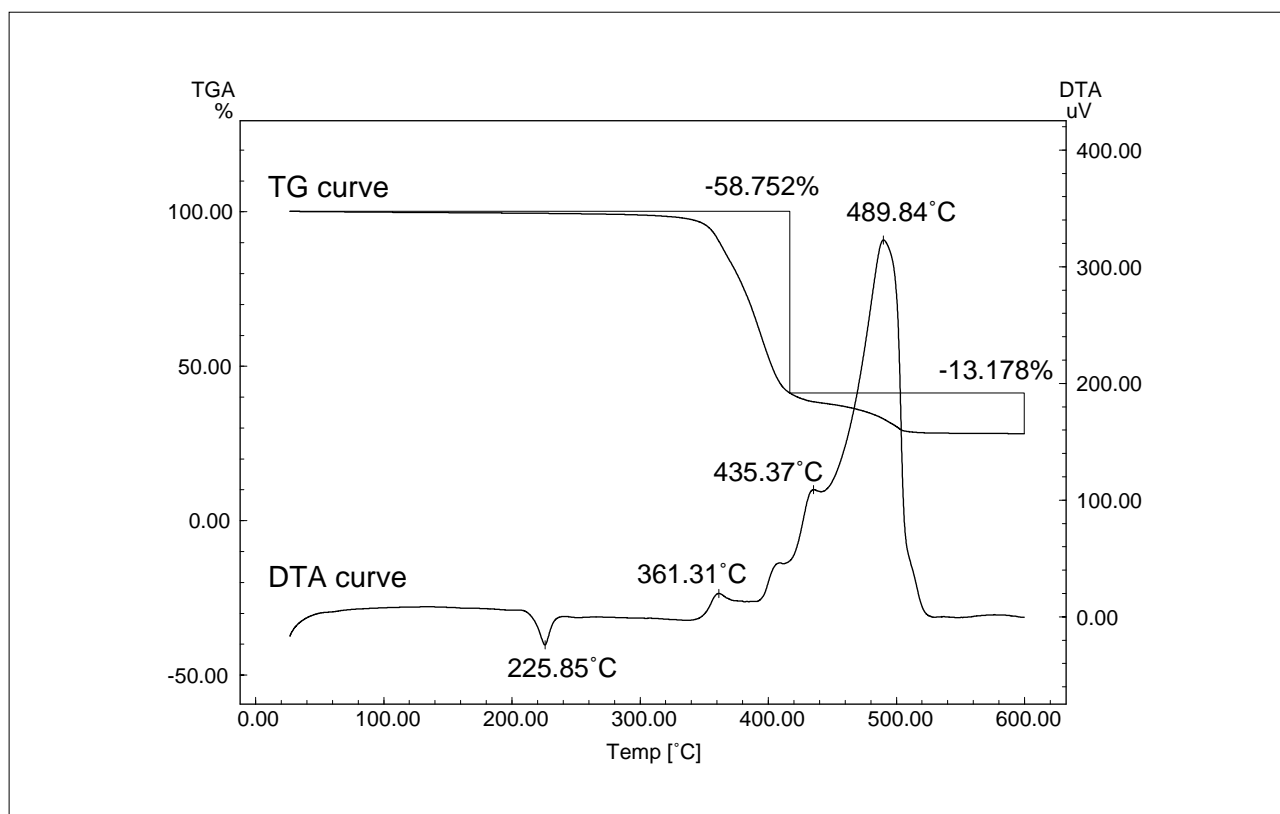


Fig. 9.2.1 TG-DTA curves of a Diode

## 9.3 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

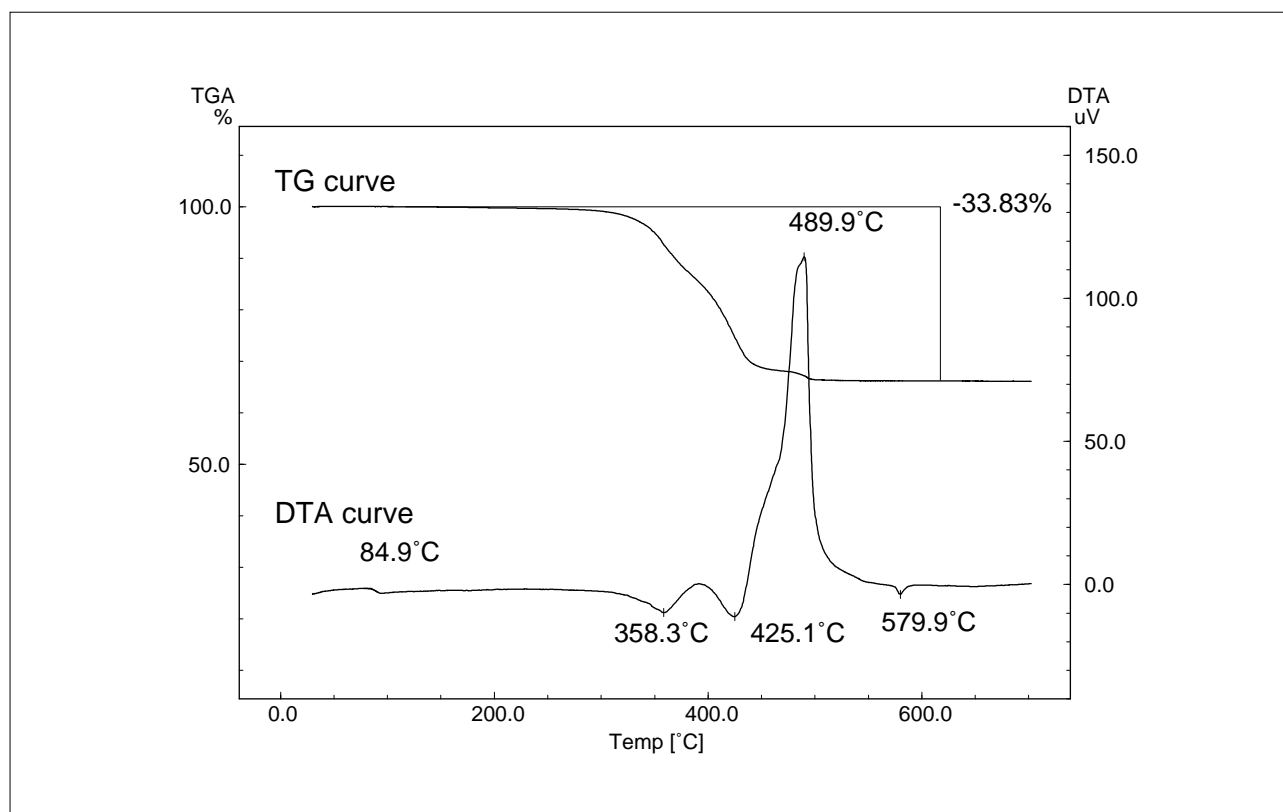


Fig. 9.3.1 Quantification of quartz in epoxy resin



## 9.4 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.9.4.1) : Solder

Sample Amount : 11.26mg

Sample (Fig.9.4.2) : Lead free solder

Sample Amount : 10.38mg

Sample (Fig.9.4.3) : Lead free solder

Sample Amount : 10.71mg

Atmospheric Gas : N<sub>2</sub>

[Temperature Program]

Heating Rate : 10°C/min

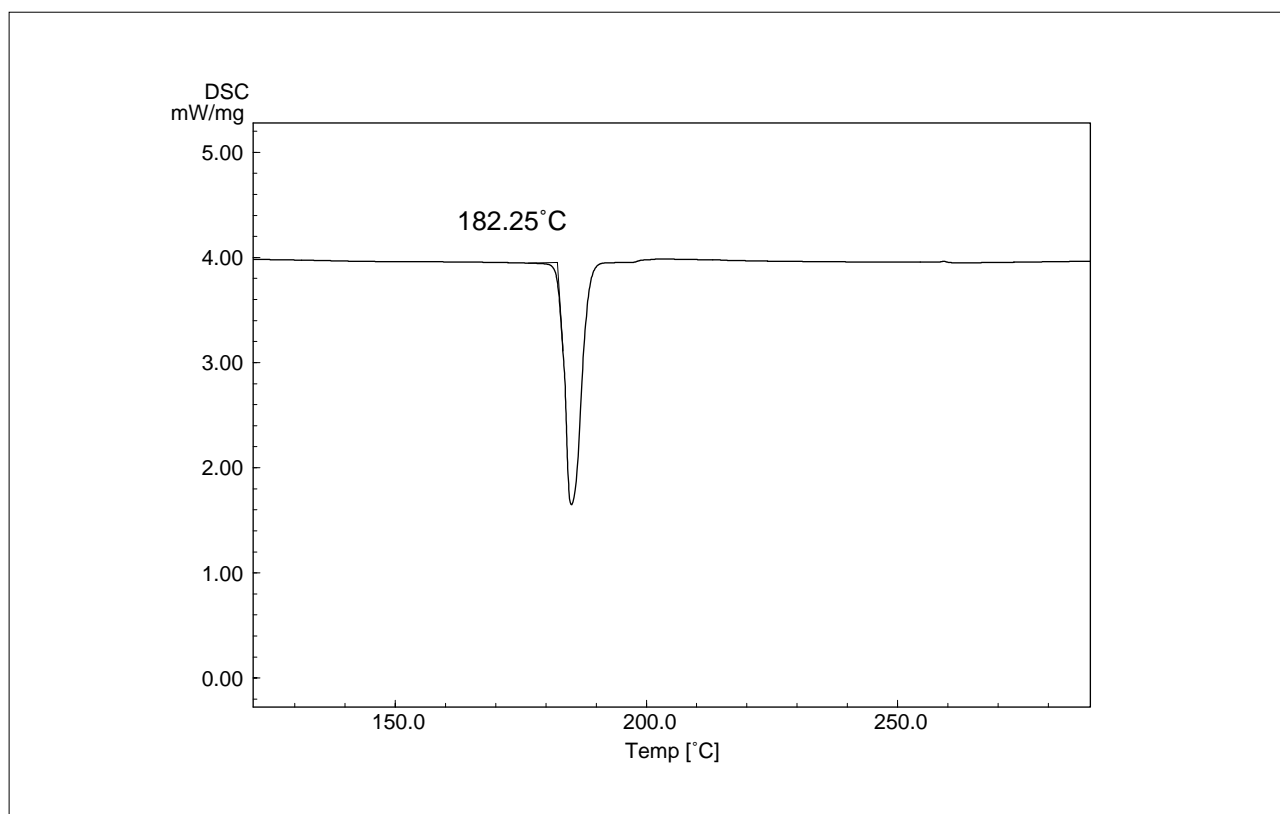


Fig. 9.4.1 DSC curve of Sn-Pb solder

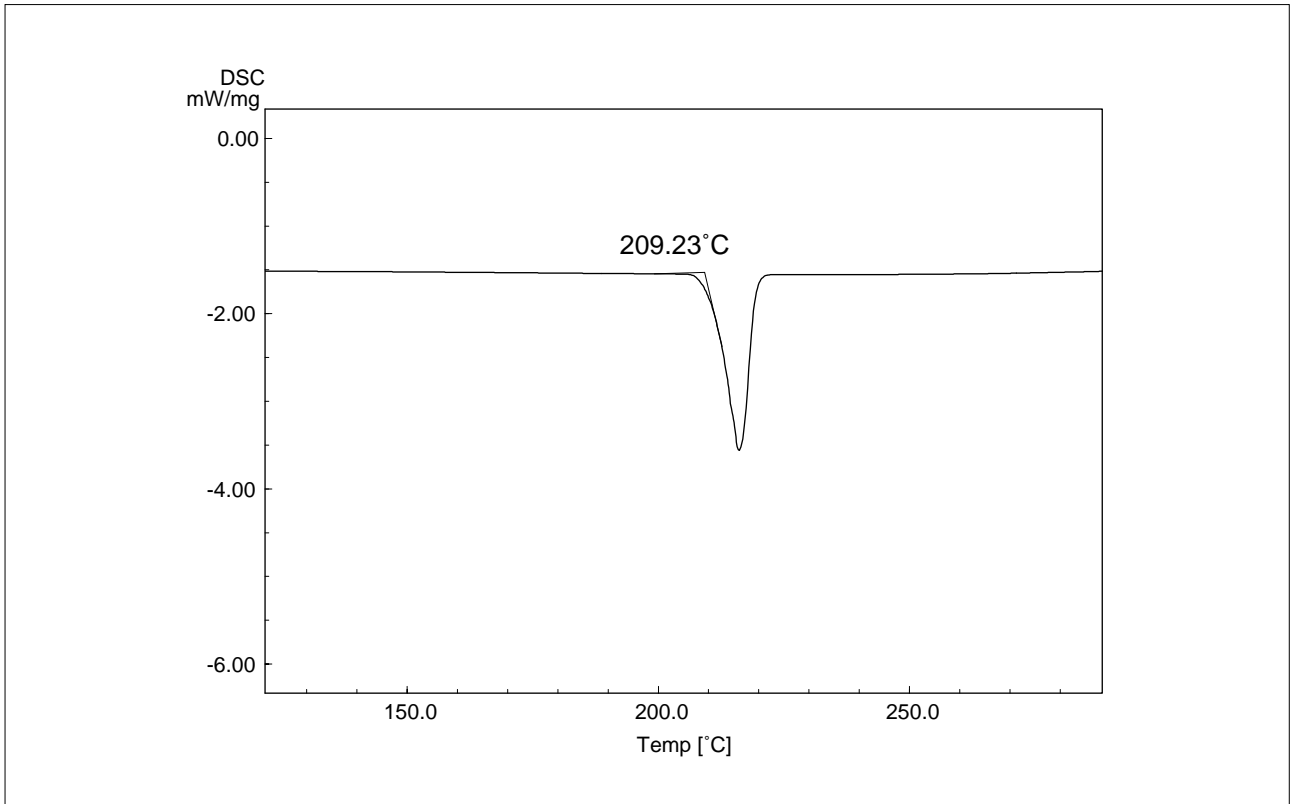


Fig. 9.4.2 DSC curve of lead free solder(Sn-Ag-Bi-Cu)

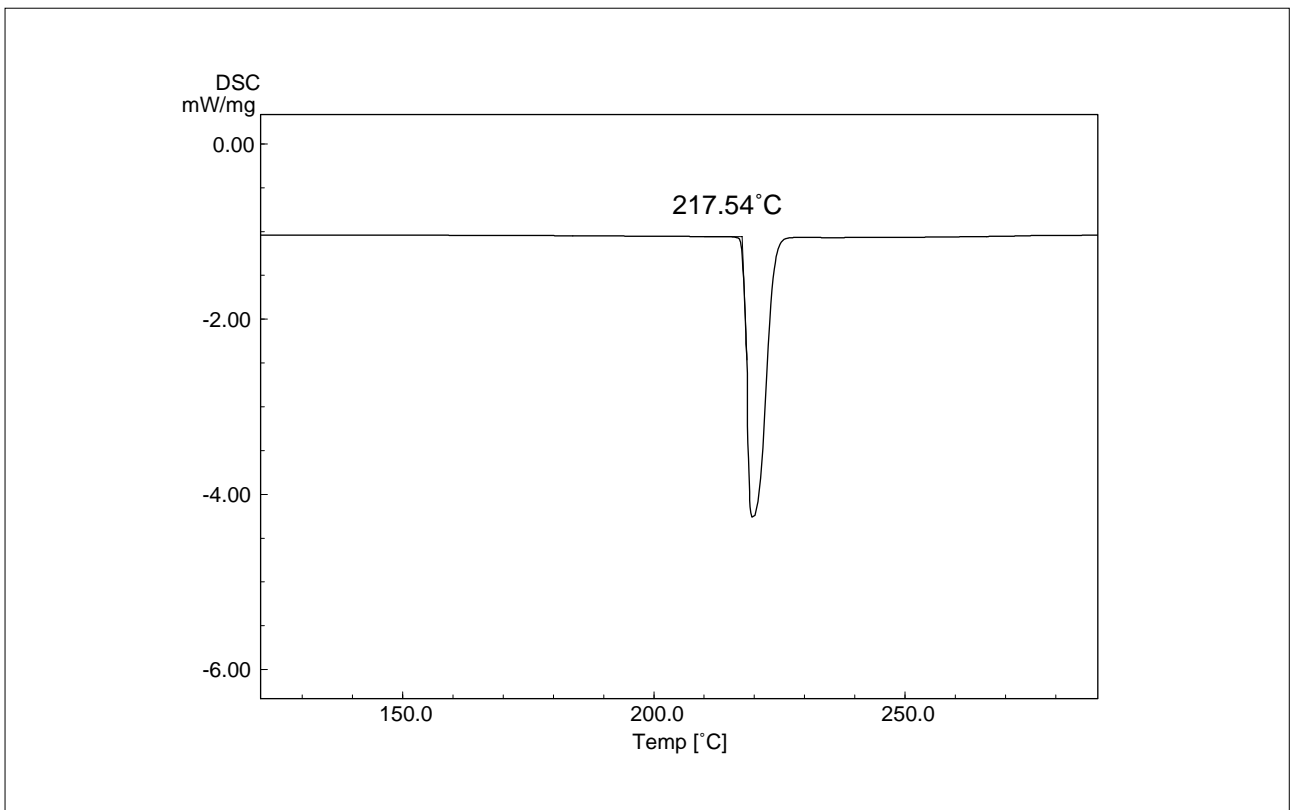
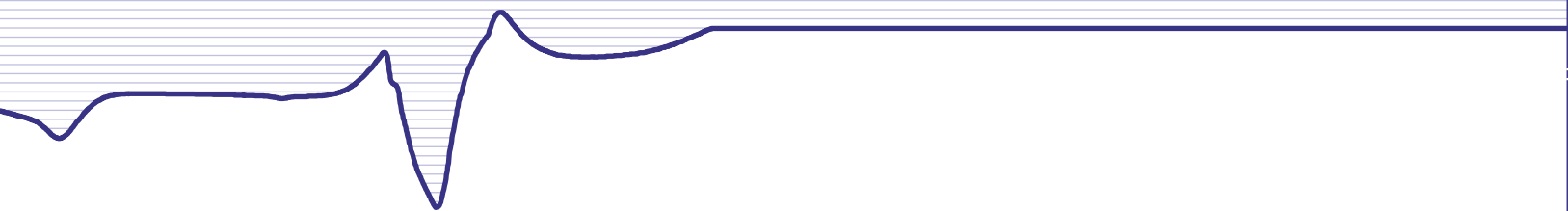


Fig. 9.4.3 DSC curve of lead free solder (Sn-Ag-Cu)



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