Technical know-how in thermal analysis measurement —Thermomechanical analysis—

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1. Introduction

The International Confederation for Thermal Analysis and Calorimetry (ICTAC) defines thermomechanical analysis (TMA) as a method of thermal analysis in which the temperature of a sample is being subjected to a defined temperature program, allowing changes, while a non-oscillatory load is being applied and that the deformation of the sample is being measured as a function of temperature or time. It is a technique that measures the dimensional changes of a sample due to heating or cooling.

The measurement results are plotted in a TMA curve where the temperature or time is plotted on the horizontal-axis, while the change in length (i.e., rate of change or expansion ratio) is plotted on the vertical-axis. In a TMA curve, an increase in the TMA measurement data represents expansion while a decrease denotes contraction. Figure 1 shows a typical TMA curve for glass.

The TMA curve shown in Fig. 1 can be divided into three regions. In the temperature range from 30 to 290°C, the glass expands linearly with increasing temperature. The expansion increases drastically from 290 to 310°C because of a glass transition. For temperature increases beyond 310°C, contraction is seen rapidly due to softening.

Using TMA, the expansion ratio and the coefficient of thermal expansion of the sample, as well as the softening temperature and glass transition temperature can be measured. The coefficient of thermal expansion (CTE) is defined as the expansion ratio per unit temperature of a calculated temperature range. The expansion ratio and the coefficient of thermal expansion of the glass at 30 to 250°C calculated from the TMA curve shown in Fig. 1 are 0.3% and $1.23\times10^{-5}\,K^{-1}$, respectively. Other TMA measurements include the determination of the sintering temperature and the volumetric contraction ratio caused by sintering of ceramic samples.

This paper summarizes effective techniques for common cases in performing TMA measurements. The overview of this paper include types of TMA measurements; differential thermal expansion principle and single expansion principle; sample preparation and sampling; sample setting; calibration and correction of measurement results; and high- accuracy measurement module.

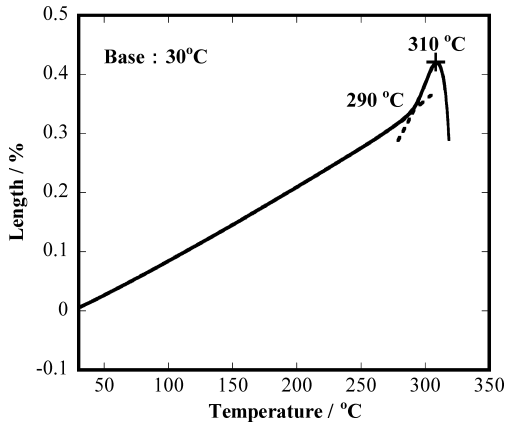

Fig. 1. TMA measurement result for glass.

2. Types of TMA measurements

In a TMA measurement, different detection rods, support pipes, and several measurement methods can be selected depending on the form of the sample and the measurement objective. There are three types of measurement methods, namely compression loading method, tensile loading method and penetration method.

2.1. Compression loading method

The compression loading method (Fig. 2) is used to measure a freestanding sample (i.e., a sample that can stand independently) such as a block, a pellet or a

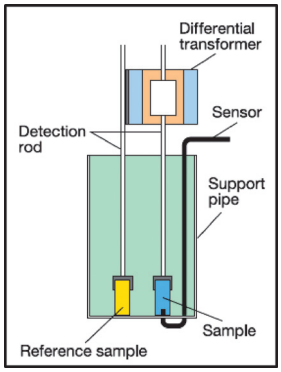

Fig. 2. Compression loading method.

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pressure-molded powder. The sample is set inside the support pipe and it is held downwards by the detection rod. The displacement of the sample is measured through the detection rod where the upper end of the rod is connected to a differential transformer. Using the differential expansion principle, simultaneously measuring the actual sample and a reference sample with a known thermal expansion cancels the thermal expansions of both the support pipe and the detection rod (details see section 3). Comparing the differential expansion principle with the single expansion principle (see section 3), the former reveals a high measurement precision and indicates to be more effective for samples with small amounts of change.

2.2. Tensile loading method

The tensile loading method (Fig. 3) is used to measure a non-freestanding sample such as a film or a fiber. The sample is fixed on a metal clamp. During a measurement, a constant tensile strength is applied while keeping the sample between the support pipe and the detection rod. The tensile loading method is mostly used for TMA measurement of polymers where the expansion ratios of polymers are much larger than those of the support pipe and the detection rod, which are both made of SiO_2 material.

2.3. Penetration method

The penetration method (Fig. 4) is used to measure the softening temperature of a sample such as a film or a sheet material. The modular structure is the same as the compression loading method described earlier. The penetration method is designed to detect sensitive changes due to softening. The pin-shaped edge of the detection rod is so designed for this purpose. In measuring the softening temperature of a thin film coated on a base material, the reference material to be set is the base material where it will cancel the expansion of the base material, allowing an accurate measurement of the thermal behavior of the thin film.

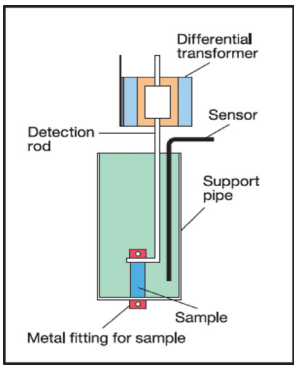

Fig. 3. Tensile loading method.

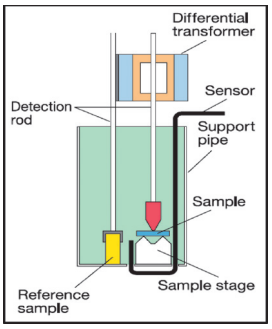

Fig. 4. Differential penetration method.

3. Differential thermal expansion principle and single expansion principle

Differential expansion principle is used in the compression loading method and penetration method. The actual sample and the reference sample are placed inside the support pipe and measured. The single expansion principle, on the other hand, is used in the tensile loading method, where only the sample is set and measured. The TMA data obtained from the measurement result is the output value of the differential transformer.

In single expansion principle, the coil of the differential transformer is stationary, therefore the TMA output value or ΔL_{TMA} is

$$\Delta L_{TMA} = \Delta L_{Sample} + \Delta L_{Detection\ rod} + \Delta L_{Support\ pipe}$$

Polymer materials are mainly measured using the tensile loading method and these materials, ΔL_{Sample}, have exceedingly larger change in expansion than those of the detection rod and the support pipe, $\Delta L_{Detection\ rod}$ and the $\Delta L_{Support\ pipe}$. Thus, the change in expansion of the detection rod and the support pipe, $\Delta L_{Detection\ rod}$ and the $\Delta L_{Support\ pipe}$, will be negligible. However, when measuring of samples with low thermal expansion coefficient, such as a ceramic or a glass sample, using the compression loading method, both the $\Delta L_{Detection\ rod}$ and the $\Delta L_{Support\ pipe}$ must be taken into account. In this case, values of $\Delta L_{Detection\ rod}$ and the $\Delta L_{Support\ pipe}$ can be subtracted using the differential expansion principle. In the differential expansion principle, the coil and the core of the differential transformer are respectively set as the reference and the sample, therefore:

$$\Delta L_{TMA} = \Delta L_{Core} - \Delta L_{Coil}$$
$$\Delta L_{Core} = \Delta L_{Sample} + \Delta L_{Detection\ rod} + \Delta L_{Support\ pipe}$$
$$\Delta L_{Coil} = \Delta L_{Reference} + \Delta L_{Detection\ rod} + \Delta L_{Support\ pipe}$$
$$\Delta L_{TMA} = \Delta L_{Sample} - \Delta L_{Reference}$$

Since both the detection rod and the support pipe are made of the same material, the $\Delta L_{Detection\ rod}$ and the $\Delta L_{Support\ pipe}$ will cancel each other. Unlike other standard thermal analysis methods, the material of the reference sample used in the TMA measurement is a material with a known thermal expansion. Hence the amount of expansion of the reference sample can be calculated using the following equation:

$$\Delta L_{\text{Sample}} = \Delta L_{\text{TMA}} + \Delta L_{\text{Reference}}$$

The amount of change in the sample can be measured accurately using the differential expansion principle. The correction method in which the expansion amount of the standard sample is added to the measurement results is called the standard sample correction. When analyzing measurement results obtained from the differential expansion principle, the standard sample correction must be carried out.

4. Sample preparation and sampling

When preparing sample materials for TMA measurement it is important to bear in mind basic precautionary measures that can affect sample measurements to obtain correct measurement results. Also, it is effective to perform a repeated measurement or a cooling measurement because thermal hysteresis can affect the measurement results.

4.1. Sample shape

In the compression loading method, it is best that the top and bottom surfaces of the sample are flat and parallel. Caution is necessary if the sample's top and bottom surfaces are neither flat nor parallel because mechanical motion (due to external vibrations or vibrations caused by instrumental robotics operation) of the detection rod may occur during a measurement. It is desirable that the top and bottom surfaces of a rectangular or cylindrical-shaped sample are, as much as possible, in right angles towards the lengthwise direction of the sample. Hence, errors can occur on the expansion measurement of a slanted sample.

Figure 5 shows the detection rod tips that can be selected to conform the sample's surface which can either be arc or flat.

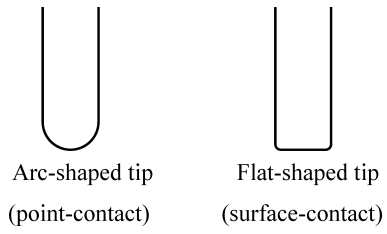

Fig. 5. Two types of detection rods.

◆ Automatic length measurement function

Measuring the initial length using the "automatic length measurement function" in the module is useful for the measurements of several samples. Measuring the initial length of the sample (the surface area of a sample where the detection rod comes into contact) after setting the sample inside the module allows an accurate initial length measurement. It is observed that the results of a measurement obtained using this function for samples with complicated shape are better than those obtained by a micrometer.

4.2. Sample preparation

During sample preparation, such as cutting a sample, the sample is vulnerable to generate thermal hysteresis and processing strain. Cutting a material (especially a polymer) with the use of scissors, nipper or coping saw may cause a change in sample properties generated by frictional heat. In this case, a new thermal hysteresis will be added on to the sample. Therefore, a sample should be cut slowly in such a way that heat is not being generated during the cutting process. Similarly, using a sand paper to level the surface of a sample or using a nipper requires careful handling because the latter can possibly cause deformation on the cutting surface.

A powder sample can either be pressure-molded to a prescribed size using a sample molding apparatus or by simply packing the powder sample in an open pan prior to measurement. It is recommended that the same sample pan should be set on the reference side so that the thermal expansion in the sample can be accurately determined.

4.3. Effects caused by measurement direction

Figure 6 shows the results on a film measured along two perpendicular directions of ***A*** and ***B*** (Fig. 6). The two TMA curves plotted in the left-hand side of Fig. 6 show an expansion in the film when measured along the ***A*** direction and a contraction in the film started from 80°C when measured along the ***B*** direction. This indicates that the film cut in the ***B*** direction was stretched. During processing, the thermally stretched film tends to restore to its former state when heated to its processing temperature. Thus, contraction is seen in the stretched direction and expansion is confirmed in the non-stretched direction.

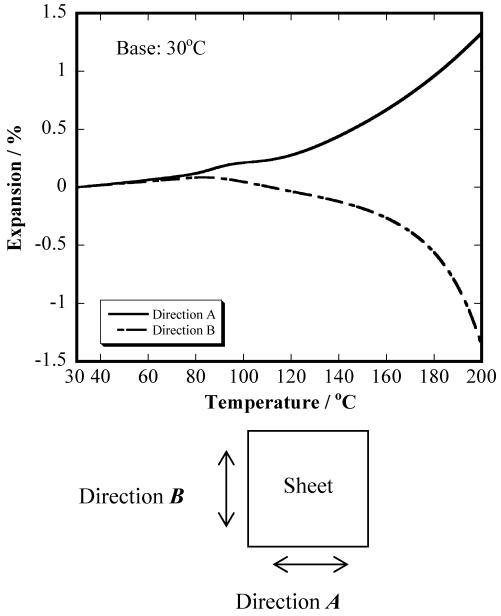

Fig. 6. Compression loading TMA measurement results of a uniaxially-stretched PET film.

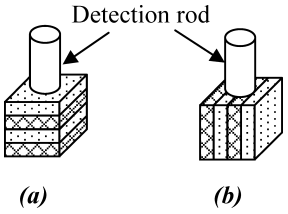

Fig. 7. Multi-layered sample.

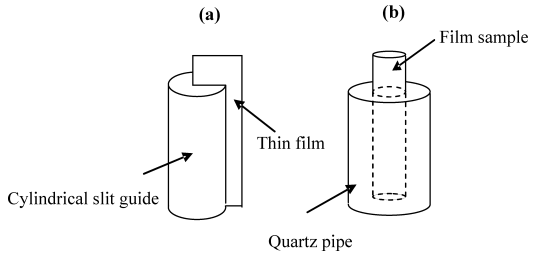

Fig. 8. Tools for measuring a thin film using compression loading method.

In a multi-layered sample such as a base-resin or a multi-layered film, TMA measurement results differ depending on the stacking/interface direction of the sample. In case (*a*) shown in Fig. 7, the sum of expansion and contraction of the stacked material is detected. Case (*b*) shows is an interaction in the change of form in the stacked material. If the differences in the amounts of change in all layers increase, it is possible that the sample may be distorted, warped or detached from the stack. In the case where fiber glass surface exists in the base resin and the expansion ratio is exceedingly smaller than the base resin, the expansion of the base resin in the fiber glass' direction will be suppressed. Therefore, the measurement results on the thermal expansion will be influenced by the measurement direction.

4.4. Effects of thermal hysteresis on a sample

As mentioned in section 4.3, thermal hysteresis may cause a change of the form of a sample. Therefore, the direction and the sampling location are two of the important factors in a TMA measurement. Also by conducting a second heating, the thermal hysteresis will be cancelled, and the change in the form of the sample can be measured. Even if the sampling location and the measurement direction are the same in a material having different thermal hysteresis, the difference in thermal hysteresis can be seen in the first heating measurement and the same results can be obtained in the second heating measurement. Furthermore, when comparing the measurement results of the second heating measurement obtained by using the same cooling process after the first heating, the results can be compared if it is measured using the same condition. In addition, in the first and second heating measurements, initial length of the sample at the start of the measurements can be different. Even though if the sample is already set inside the module, it is effective to use the automatic length measurement function beforehand. For this reason, the initial length of the sample in the second heating measurement will also be measured accurately. The automatic length measurement function should be used in advance to ensure an accurate measurement of the initial length of the sample prior to the second heating measurement.

- **The effect of thermal hysteresis in the second heating measurement**

The thermal hysteresis that exists in a sample will be cancelled during the first heating measurement. However, a new thermal hysteresis will be generated during the cooling process. When comparing the second heating measurement, there is a need to standardize the cooling condition to ensure that it will have the same thermal hysteresis. It should be noted that the same thermal hysteresis should be applied to the same sample. Using an automatic cooling system enables a recycle measurement, or automatically setting the cooling fan at the end of the measurement is useful to achieve a constant cooling condition at each measurement.

5. Sample setting

5.1. Measurement of a thin sample with the compression loading method

As mentioned in Section 2.1, the compression loading method is used for measuring a freestanding sample. A measurement of a non-freestanding sample is also possible if the sample can become stable and freestanding when a load is applied.

Sheet material can be measured by inserting the sample into a cylindrical-slit guide (sheet sample guide) to keep and hold the sample (Fig. 8(a)) in place. For a film sample, it is best to roll the sample and insert the sample into a quartz pipe (Fig. 8(b)). It should be noted that the sample must be carefully handled to avoid sample bending or the ccarrence of possible friction between the sample and the tool.

5.2. Handling complicated samples with metal clamp

In a tensile loading measurement, a brittle sample may break when fastened with a metal clamp. The force applied to the fragile sample during clamping can be reduced when a soft material such as aluminum foil or a paper tape is inserted between the contact area of the sample and the metal clamp. This method can also be used for an exceedingly thin sample which may slip from the metal clamp.

5.3. Fusion-bonding prevention on the detection rod and support pipe

When measuring a ceramic or glass material, fusion-bonding may occur on the detection rod and support pipe. The damage on the detection rod and support pipe may be prevented by inserting an Al_2O_3 or SiO_2 plate on the upper and lower surface of the sample

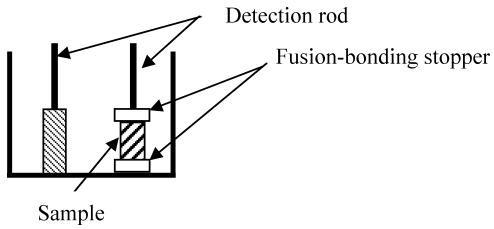

Fig. 9. A setting example of fusion-bonding stopper.

(see Fig. 9). Furthermore, when measuring the softening temperature of a glass sample, a function called "meltdown protection function" can be used to prevent fusion-bonding due to softening. With this function, the measurement ceases automatically when the amount of changes reaches the preset values during measurement and therefore preventing a possible damage caused by melting beforehand.

◆ **Protection from decomposition gas**

During a TMA measurement, the evolution of gas due to reactions, such as decomposition, may occur. In this case, a gas flow can be used to prevent the evolved gases being flowed to the balance room (upper part of the module) and keeps the partial pressure constant. The effect of contamination will be reduced substantially if a rapid elimination of gases from the system will be done even when the support pipe and the detection rod are already contaminated.

6. Calibration and correction of measurement results

Calibration and correction of measurement results are highly recommended so that possible errors due to equipment condition, degradation and/or TMA principle dependent error margin can be kept to a minimum. Especially in the case of using several modules in a measurement, it is best that the calibrated and corrected data are compared.

6.1. Baseline (blank) measurement

First the module's condition should be confirmed by measuring the baseline prior to determine the precision and accuracy of the measurement results. Measuring the baseline can confirm possible thermal drift of the TMA module used for a measurement. The baseline measurement is done using a reference sample with the same length. The reference sample is set in the sample and the reference sides inside the support pipe and measured using the same measurement condition of the actual sample. In this measurement, if the reproducibility of observed expansion or contraction can be confirmed, then by correcting the measurement results, accurate values for the actual sample can be obtained. The reproducibility of the baseline measurement plays an important role when discussing the accuracy of the module.

6.2. Temperature calibration

The temperature measurement in TMA is mostly carried out in the vicinity of a sample, and there can be a slight difference in temperature between the sample and the reference. When discussing the accuracy of the temperature, the melting of more than 3 different standard samples with known melting points are measured prior to performing a temperature calibration. In calibrating a specific temperature region, the use of a standard sample with the nearest melting point in the temperature region is desired, and this can increase the accuracy of the calibration. A fusion stopper plate should be used when measuring the melting of a metal sample (see section 5.3).

6.3. Literature value correction

Comparing TMA with other thermal analysis modules such as TG-DTA and DSC, TMA is used for the measurement of a volumetrically large sample, for a sample with low thermal conductivity in which the temperature distribution within the sample increases easily. Especially when the measurement objective is either thermal expansion ratio or coefficient of thermal expansion, performing a temperature calibration could be insufficient. In this case, a standard material with known expansion ratio is measured, and then a correction factor can be determined from the difference in the literature value. The correction factor used for correcting is called literature-value correction. The standard sample used should be made from a material with a known expansion ratio. Since the objective is focused on the correction of the temperature distribution within a sample, the reference sample should have a similar thermal conductivity with the sample. In a metal sample, Pt and Si are commonly used as standard materials, while the c-axis of a sapphire standard is commonly used in a TMA analysis of an oxidized sample.

7. High- accuracy measurement module

In the case of a high-accuracy TMA measurement of a material with low expansion, expansion ratio and coefficient of thermal expansion, a horizontal type TMA is recommended. A horizontal type TMA can measure a sample with a length up to 50 mm, and its detectable amount of change is 2.5 times better than that of a vertical type TMA. If the sample's length is long, the amount of change in the sample can easily be detected. Therefore, a horizontal-type TMA can obtain a highly accurate measurement result than those of a vertical type-TMA.

8. Conclusions

The precision and accuracy of TMA measurement results largely depend on the form and on the pre-treatments such as preparation of a sample. If an ideal sampling condition has been carried out, accurate TMA measurement results can be obtained. In relation to the form of a sample as well as the objective of a TMA measurement, sampling becomes important in achieving accurate measurement results.