Reviews

Thermal Analysis—as a Method of Material Characterization
A Review

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The use of thermal analysis as a method for material characterization is increasing, particularly in the development of new materials. This review describes three of the analytical techniques within thermal analysis: differential scanning calorimetry (DSC), thermomechanical analysis (TMA) and dynamic mechanical spectrometry (DMS). DSC and TMA are the traditional thermal analysis techniques, and have gained wide acceptance for material characterization. Specific heat capacity measurements using the DSC and thermal expansion coefficient measurements using the TMA are discussed. This review also includes a discussion of the DMS as a newly added technique in thermal analysis and its application to polymers.

Keywords Differential scanning calorimetry, thermomechanical analysis, dynamic mechanical spectrometry, enthalpy method, scanning method, temperature dispersion, thermal expansion coefficient

1 Introduction

Thermal analysis is a generic term which encompasses several analytical methods. Each analytical method has precise definitions for its designations, abbreviations, acronyms, technical vocabulary and classifications. These definitions were established by the International Confederation of Thermal Analysis (ICTA), and continue to be observed today. Table 1 lists the characteristic analytical methods and equipment used in thermal analysis. A practical computer application has helped to expand marketed equipment to correspond to the above mentioned classifications; consequently, the thermal analyzer has become compatible with other analytical systems.

In recent years the development of new materials has been actively pursued. This ongoing search is indispensable for the improvement of high-temperature stability, mechanical strength and material characterization, particularly in the electronics and automobile industries. Analytical methods in thermal analysis are suitable for assessing the unique characteristics of new materials. Furthermore, the thermal analyzer has been developed for practical use in new fields and for improvements in basic analytical precision pertaining to the needs of new-material scientists. Under these circumstances two new trends are taking place. The first is advancement through combining analytical methods (i.e., Fourier transform infrared spectrometry and differential scanning calorimetry, Fourier transform infrared spectrometry and thermogravimetry, gas chromatography/mass spectrometry and thermogravimetry). The second advancement concerns equipment and techniques for determining the exact physical properties of matter.

The overall progress of thermal analysis is stated in Dollimore’s Review. The focus of this review includes the following subjects: multi-phased assessments of new material properties; specific heat capacity measurements using the differential scanning calorimeter (DSC); thermal expansion coefficient measurements using the thermomechanical analyzer (TMA); and viscoelasticity measurements using the dynamic mechanical spectrometer (DMS). Practical illustrations are included.

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Keywords: Differential scanning calorimetry, thermomechanical analysis, dynamic mechanical spectrometry, enthalpy method, scanning method, temperature dispersion, thermal expansion coefficient.
2 Specific Heat Capacity Measurements Using the Differential Scanning Calorimetry

2-1 Differential scanning calorimeter

The differential scanning calorimeter (DSC) has two heat-flow detecting methods: the power compensation method and the heat flux method. Figure 1 is a conceptualization of the different detector configurations. The DSC measures the difference in the heat flow between the sample to be tested and a known standard. The samples are kept at the same temperature through the use of an automatic compensator that senses any difference in temperature and makes appropriate adjustments. The heat compensation value is recorded as the thermal flow growth rate. The difference in these two methods is that one uses a direct heat compensation with a heat sink, while the other measures the difference between two individually arranged heaters. Recent experimentation with the measurement principles of the DSC power compensation and heat flux methods has been uniformly conducted and has clarified the meaning of the respective curves.7,8

A cooling apparatus must be used when making low-temperature DSC measurements. Many types of cooling equipment have been designed and put on the market. Since it is essential that DSC data for specific-heat capacity measurements be reproducible, there is a demand for accurate cooling equipment. Figure 2 shows an example of a DSC and cooling unit combined for measuring the low-temperature specific heat capacity.4 In this example, a heating unit is included in the detector mechanism and the entire unit is immersed in nitrogen gas coolant. To improve the reproducibility of measurements, the cooling device remains in place while measuring the specific-heat capacity. The cooling gas flow is controlled by a computer as a function of the temperature and the heating/cooling rate, while a typical control system uses only a heater. Using this method, the temperature control system with an ordinary heater can work as a dual control system.
2.2 Measurement of specific heat capacity

Until recently, measurements of the specific-heat capacity using the adiabatic method has been both accurate and highly standardized. Nevertheless, the DSC is also being utilized for heat-capacity measurements because of its improved ability to accurately reproduce data. The DSC method for measuring the specific-heat capacity is classified into two types: scanning and enthalpy. With the scanning method, calculations are made by comparing DSC signals: the sample, reference (material with a known heat capacity), and blank curves. The ratio of \(H\) and \(h\) in Fig. 3(a) is proportional to the ratio of the sample heat capacity and the reference heat capacity.

With a series of short step-like heat increases, the enthalpy method is calculated from the area encompassed by the DSC signal, the isothermal base line and the height of one step (see Fig. 3(b)). Mraw and Naas compared the precision of the scanning method using power compensation DSC with the enthalpy method, and determined that within a temperature range of 27 to 427°C both methods have an accuracy of ±1%.10,11 However, the data variance of the enthalpy method is smaller than that of the scanning method. From these results it cannot be reliably stated that the enthalpy is the superior method. Still, Mraw and Naas' recommendation of the enthalpy method is not based on an inconclusive point, such as that of the inferiority of the sample temperature change during the scanning process. A report based on tests of commercial equipment noted improvements in the accuracy of specific-heat capacity measurements with the enthalpy method.12 It is believed that the effectiveness of the enthalpy method depends on the structure of the equipment, particularly that of the temperature-measuring unit. It is reported that the enthalpy method has an accuracy of 0.6% and the scanning method an accuracy of 5.0%.

By decreasing the temperature step-height, and by taking sufficient time for isothermal maintenance, it is possible for measurements to be taken in a state of near thermal equilibrium. Claudy concluded that glycerol's specific heat capacity is reversible within the glass transition region by utilizing the enthalpy method, heating by 2°C temperature steps, and then cooling.13 Furthermore, the accuracy agrees within 3.0% of the value obtained using the adiabatic method.

There are two superior points regarding the measurement of the specific-heat capacity with the DSC: the ability to delicately and freely create the conditions of heating and cooling, and the ability to easily create a sample history. These conditions are indispensable when the object of measurement is a polymeric sample with large property changes in its thermal history. The scanning method used by DSC has been adapted by the Japanese Industrial Standard (JIS) as the standard method for measuring the specific-heat capacity of plastics.14,15 The author used this scanning method and reported on accuracy changes under various conditions.

![Fig. 3 Schematic DSC curves for heat capacity calculation. (a), scanning method; (b), enthalpy method. The shaded area is proportional to the enthalpy increment between the initial and the final equilibrium temperatures.](image)

![Fig. 4 Relationship between RSD (%) of heat capacity and heating/cooling rate. Test sample, sapphire pellet; temperature, 100°C. □, 20 mg heating data; ●, 50 mg heating data; ×, 30 mg cooling data.](image)
Capacity can be determined with an accuracy of 1.5%, within a temperature range of -150°C to 700°C. Furthermore, the accuracy when in a cooling state is the same as when in a heating state. Measuring the specific-heat capacity while in a cooling state has practical applications in phase-transition research, in the research of the properties of supercooled materials, and in the research of the relaxation process of polymers.

Wunderlich and others are increasing the accuracy of specific-heat capacity measurements by placing the sample pan at the same spot each time. They have reported a measurable accuracy of ±0.3% in the temperature range from room temperature to 300°C, along with a sample placement accuracy of ±0.5 mm using an auto sampler (arm-robot type). Future applications of the arm-robot toward improving specific-heat capacity measurements should be significant.

### Figure 5
Relationship between RSD (%) of heat capacity and heating interval. Test sample, sapphire pellet 30 mg; heating/cooling rate, 10°C/min. O, 600°C; ●, 400°C.

### Figure 6
Relationship between RSD (%) of heat capacity and temperature. Test sample, sapphire pellet 30 mg; heating/cooling rate, 10°C/min. O, heating data; ●, cooling data.

### 3 Measurement of the Thermal Expansion Coefficient Using Thermomechanical Analysis

#### 3.1 Thermomechanical analyzer
According to the ICTA definition, thermomechanical analysis and measurement of the thermal expansion coefficient are defined separately, even though the construction of the pushrod method (measurement of the thermal expansion coefficient), and the thermomechanical analyzer are similar in type. A thermomechanical analyzer is commonly used to measure the thermal expansion coefficient. By creating a load on the probe, and exchanging the probe to one that can sense alterations in the sample dimensions, the TMA can correspond to various measurement techniques, including: the thermal-expansion coefficient, softening point, tension and creep. Figure 7 shows the TMA structure and Fig. 8 shows various types of probes. Table 2 indicates which TMA measurement techniques corresponds to each load and temperature condition. The

### Figure 7
Schematic diagram of TMS apparatus.

### Figure 8
TMA probes for each TMA techniques.
method used for creating loads within the structure has been greatly improved in recent years. The electromagnetic force has replaced gravity as a counter weight, and the load is now freely controlled by a computer. With certain available equipment it is now possible to create a load as small as 10 mg. Furthermore, the force for preserving a fixed sample length can now be observed and used in thermal contraction stress and stress relaxation measurements.

The physical structure of the TMA remains fairly constant up to 1000°C, but changes greatly when the temperature exceeds 1000°C. A major factor is whether or not fused quartz, which has a small expansion coefficient, can be used to make sample holders and probes. Fused quartz can be used at temperatures up to 1000°C; however, given the deterioration rate over time, quartz cannot be used at temperatures higher than 1000°C.

It is consequently necessary to use materials like alumina ceramics which have an expansion coefficient ten times that of fused quartz. It is also necessary to revise the original expansion rate correction for materials used in constructing the apparatus. There is a possibility of using highly purified alumina as the structural material for temperatures up to 1700°C. The JIS R-type thermocouple is used up to 1500°C in machinery and tools. The TMA is seldom used above 1500°C. For measurements of the thermal-expansion coefficient in low-temperature regions it is desirable to use an apparatus equipped with a cooling device similar to the DSC which can accurately control the temperature. Furthermore, to maintain the accuracy of temperature measurements, thermocouple lead wires must be carefully designed to prevent thermal leaks. Most of the TMAs presently on the market are designed for measurements starting at -150°C.

### 3-2 Thermal expansion coefficient measurement

The main methods for measuring the thermal-expansion coefficient include TMA-pushrod, X-ray diffraction and optical interference. However, the TMA method, with relatively few limitations on the size and the nature of the sample, is widely used. There is currently a movement to make the TMA method the industry standard. Also, the TMA method for measuring the thermal-expansion coefficient of cast iron is being studied for inclusion into the JIS. A study regarding the accuracy of the TMA method for measuring the thermal-expansion coefficient will be presented at a symposium sponsored by the ASTM in March 1990.

To improve the accuracy of measuring materials that have a small expansion coefficient, it is necessary to base corrections on the original measurement theories. In looking at such theories, it is known that the TMA method requires a reference sample that has a well-known expansion coefficient. In the end, it is the reproducibility of the length and temperature measurements that determines measurement accuracy. The formula for calculating the thermal-expansion coefficient and the correction method are outlined below.

The following formula is used to calculate the thermal expansion coefficient from TMA data:

\[ \beta = \frac{\Delta L}{L_0(T_2 - T_1)} \]

where \( T \) is the temperature, \( \beta \) the average thermal expansion coefficient from \( T_1 \) to \( T_2 \), \( L_0 \) the initial sample length, and \( \Delta L \) the average amount of thermal expansion from \( T_1 \) to \( T_2 \).

Three common errors that occur when using Eq. (1) include: 1) errors in measuring the original sample length; 2) errors in measuring the change in sample length; and 3) errors in measuring the temperature change. Keeping the sample length measurement error under 0.1% is not difficult and is not a major cause of errors in the thermal-expansion coefficient. However, there are many possible causes of thermal-expansion coefficient measurement errors. Figure 9 shows that such errors can be eliminated by correcting for the thermal-expansion coefficient of the sample holder (reference correction), and also by correcting for the difference between part (a) of the probe and part (b) of the sample holder (blank correction). The correcting concept of the differential TMA is the same as with a typical TMA. The reference correction is calculated from the expansion qualities of the probe material, and the blank correction is calculated from the expansion coefficient data of a well-known substance. The National Bureau of Standards (NBS) supplies four kinds of materials that have known thermal expansion coefficients: tungsten, borosilicate glass, fused silica and stainless steel.

Errors in the measurement of temperature change appear as a disparity with the actual value of the thermal expansion coefficient. This disparity originates
from the difference between the average temperature of the sample and the temperature of the thermocouple used for the temperature measurement. Four methods for reducing this kind of error are listed below: 1) maintain a slow heating rate, (the uniformity of the temperature distribution around the sample is maintained); 2) use an average value when measuring the thermal expansion coefficient for heating and cooling; 3) reduce any heat loss from the temperature sensing thermocouple; and 4) calibrate the thermocouple by using the melting point of a highly purified metal as a temperature reference. The gas flow and heating rates should be set the same as in an unknown sample measurement. There are limits to the accuracy of this kind of calibration because of the temperature distribution in the sample and the effect of the sample length on the average temperature. This restricts improvements in the measurement accuracy of the thermal-expansion coefficient. The accuracy of the thermal-expansion coefficient achieved by using TMA is shown in Table 3.

### Table 3 Accuracy of expansion coefficient

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<th>Method</th>
<th>Above ambient</th>
<th>Below ambient</th>
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</thead>
<tbody>
<tr>
<td>Repeatability</td>
<td>within 0.7%</td>
<td>within 1%</td>
</tr>
<tr>
<td></td>
<td>within 2%</td>
<td></td>
</tr>
<tr>
<td>Accuracy</td>
<td>1% + 6 x 10^-4</td>
<td>2% + 3 x 10^-7</td>
</tr>
<tr>
<td></td>
<td>2% + 3 x 10^-7</td>
<td>°C</td>
</tr>
</tbody>
</table>

a. \( \Delta T \): a temperature interval \((T_2 - T_1)\) on Eq. (1).

Fig. 9 Schematic drawings of TMA. 

Fig. 10 Schematic drawing of dynamic mechanical spectrometer.
high frequencies, a light probe, flexible support equipment and an appropriate computer controlled design are very effective with DMS equipment. Measurement signals (cyclic force, cyclic displacement) in DMS equipment are calculated and converted into a real and an imaginary modulus. This is particularly true in the tension mode, where computer control maintains the sample tension by applying a stress to the sample.

4.2 Applications

The viscoelasticity measurement technique is widely known in the rheology field. Its use in the research of matter differs from the analytical methods generally described. However, if looked at from an application point of view, it can be seen as another technique for thermal analysis, because of its complementary relationship with the DSC method. DSC has a higher detection ability in the first-order phase transition, while the DMS has a higher detection ability in the glass-transition phase area.

Figure 13 shows a viscoelasticity measurement of a block copolymer sample made from SBR rubber and polystyrene. The high-temperature side originates in the polystyrene glass transition and the low-temperature side originates in the rubber component glass transition, thus showing two clear glass transition regions. The tan δ peak of the high-temperature side is lower than the single-component polystyrene glass transition temperature; since the temperature range of the peak is wide, it can be thought of as a block boundary with a mixed composition. This is one example of an evaluation method for complex polymers.

There are many examples which show the practical applications of viscoelasticity measuring equipment with polymeric material. One reason for this is that polymer structures change easily with the surrounding environment. In recent years the electronics industry has increased its demand for precision materials. Viscoelasticity is important as one way to understand structural changes. Shi used viscoelasticity measuring equipment to observe changes in solder, widely used in...
the electronics industry.\textsuperscript{28} Figure 14 shows Young's-modulus data for lead-tin alloys during the annealing process and the storage modulus change with the annealing time at room temperature. When the annealing time is around 90 d it becomes a constant value. This shows that the structure stabilizes after 90 d of continued structural relaxation.

5 Other Thermal Analytical Methods for Property Evaluation

Both TMA and DMS are used in measuring the dynamic properties of matter. The dielectric thermal analysis, (DETA) is also one of the techniques used for property evaluation, although it is used to analyze the electrical properties of a substance.\textsuperscript{29}

Since the principle of the dielectric constant (permittivity) measurement is based on the same theoretical system as the elastic modulus measurement, results reflected by molecular motion are obtained. The big difference is that dielectric constant measurements are limited, for the most part, to polarized molecules. Figure 15 shows the curing process measurements for an epoxy resin.\textsuperscript{30} In this case, the detection sensitivity of DETA is higher than that of a modulus measurement.\textsuperscript{31} Figure 16 shows a typical DETA apparatus. Similarly, a thermal-stimulated current (TSC) measurement is used as a technique to observe the electrical properties caused by molecular motion. The configuration of the equipment used is shown in Fig. 17.\textsuperscript{32} With the TSC, an electrical field is first applied to the sample (the sample being in a rubberized state); the sample is then supercooled. Subsequently, the sample is released from this "frozen" state by the activity of heated molecules; the electrical current generated is measured, and the change in molecular motion is captured. In theory, even though the detection sensitivity of molecular motion is high, since a pretreatment of the sample is required, it is not suitable for general-purpose use.\textsuperscript{33}

6 Summary

This review has covered a few of the thermal analytical techniques used to evaluate the physical properties of matter. Focusing on heat capacity and thermal-expansion measurements, the accuracy and applications concerning the DSC and TMA methods were discussed. Examples of data and special characteristic for DMS, DETA and TSC methods, which have expanded in recent years as thermal analytical methods, were also given.
Thermal analysis, which began in the late 19th century with the experimentation of Le Chatelier, has evolved along with the development of new materials. Accompanying the development of new materials and precisely controlled material characteristics, new methods of practical application will yield new analytical techniques in thermal analysis. Thermal analysis will play an even more important role in the field of material evaluation and can be thought of as many techniques within one analytical method.

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References


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