

Technical know-how in thermal analysis measurement

—Controlled-rate thermal analysis (Dynamic TG & Dynamic TMA)—

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1. Introduction

According to the International Confederation for Thermal Analysis and Calorimetry (ICTAC), thermal analysis is a group of techniques in which the material to be analyzed is subjected to a defined temperature program, and the change in the physical/chemical property of the material is measured as a function of temperature and/or time. In the defined temperature program, the temperature is controlled and programmed as a function of time, temperature change per unit time (i.e., heating rate, °C/min) or the holding time at a fixed temperature. On the other hand, the control system in the controlled-rate thermal analysis (CRTA) is not the temperature but the rate of change in a sample. For example, the sample's mass-loss rate in the controlled-rate TG (or Dynamic TG) or the rate of change of a dimension (e.g., the contraction rate) of a sample in the controlled-rate TMA (or Dynamic TMA) is controlled and measured as a parameter in this technique.

2. Condition setting

In the conventional thermal analysis, the temperature as a function of time, such as the heating rate, is the control parameter. In the CRTA, the sample's mass-change rate or rate of contraction change is the control parameter.

2.1. Measurement mode

When the rate of change in an analysis is selected, the type of a control program to be used is determined by the measurement mode. There are several measurement modes for Dynamic TG and Dynamic TMA. The descriptions of these experimental modes are given below.

2.2. Dynamic TG

There are three measurement modes, namely SIA, DRC and CRC, for Dynamic TG.

- Stepwise isothermal analysis mode (SIA)

In this mode, when the sample's mass-change rate becomes larger than the preset change rate, the temperature-hold control will begin to regulate the temperature so that the sample's mass-change rate can maintain at the preset change rate. This temperature-control process will repeat continuously during the measurement.

- Dynamic rate control mode (DRC)

Similar to the SIA mode, the temperature-hold control will begin to operate in the DRC mode when the sample's rate in mass-change becomes larger, but an increase in control also in the heating rate will start automatically in response to a decline in the sample's change rate. In the SIA mode, heating will be done using the pre-determined heating rate even in temperatures where there are no changes in the sample. But in the DRC mode, if there are no changes in the sample, heating will be done using the maximum heating rate. For this reason, the DRC features a shorter measurement time than the SIA.

- Constant rate control mode (CRC)

In this mode, temperature control is used to keep a constant mass-change rate. The cooling control will also be used when necessary. In a CRC measurement, the TG curve is linearly, and the temperature curve is nonlinear when the reaction progresses at a constant mass-change rate.

2.3. Dynamic TMA

Dynamic TMA is a technique where the contraction rate (or the rate of change of a dimension) caused by the sintering process in a ceramic material is used as a parameter when temperature control is in operation. There are two measurement modes:

- Constant contraction-rate sintering mode
- Quadratic function contraction-control sintering mode

3. Dynamic TG

3.1. Selection of a measurement mode

Among the three types of measurement modes, namely SIA, DRC and CRC, the use of the CRC mode is recommended. In the CRC mode, the temperature curve is accurately measured when the sample's reaction rate is kept constant. In a zero-order reaction such as sublimation or evaporation, the reaction proceeds at a constant temperature. In polymers where immediately after low molecularization by a random session reaction associated with degradation, the temperature will decrease.

3.2. Determining change rate

In Dynamic TG, it is necessary to select an appropriate mass-change rate. This is similar to selecting a heating rate in the conventional thermal analysis. In thermal analysis, an increase in the heating rate will

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result in a shorter measurement time. On the other hand, a decrease in the heating rate will improve the measurement resolution. Similarly, an increase in the mass-change rate will shorten the measurement time, and a decrease in the mass-change rate will improve the measurement resolution. In performing a Dynamic TG measurement, the noise level of the module becomes an important factor for consideration. An accurate Dynamic TG measurement cannot be obtained if the mass-change rate is set too low that the effect of the noise cannot be overcome.

In a measurement, the limit value of the rate is directly related to the sample's weight. The following equation is commonly used for determining the rate limit:

$$W \cdot R = 0.01 \sim 0.03$$

Where, W =weight of the sample (mg), R =change rate, %/s or %/m.

In the case of a 10-mg sample, the change rate is normally set higher than $R=0.001 \sim 0.003\%/s$ to overcome the effect of the noise. In here, $0.01 \sim 0.03$ are specified because the noise level varies depending on the condition of the module and the measurement environment (such as gas flow), and it is necessary to take both factors into consideration. In order that the noise level will be constant in the same module and in the same measurement condition, an increase in the sample amount and/or a decrease in the change rate may be required.

4. Effectiveness of Dynamic TG

4.1. Improvement in resolution

Figure 1 shows the Dynamic TG (CRC mode) curves of weight (wt.%) as well as temperature as a function of time in cyclodextrin. The TG curve plotted in Fig. 1 shows that the sample weight decreases linearly while the temperature increases nonlinearly. Figure 2 shows the multi-plot of Dynamic TG and conventional TG obtained with a constant heating rate of $10^\circ\text{C}/\text{min}$ as a function of temperature. The constant heating rate curve shows that there are a number of continuous reactions, and these reactions are difficult to be quantified

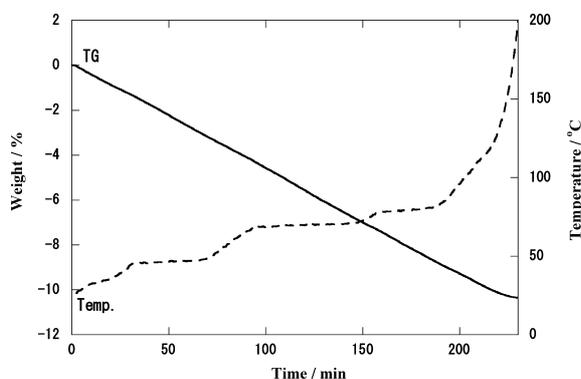


Fig. 1. Dynamic TG (CRC mode) data of a 20-mg cyclodextrin sample with a constant $0.03\%/min$ weight loss rate.

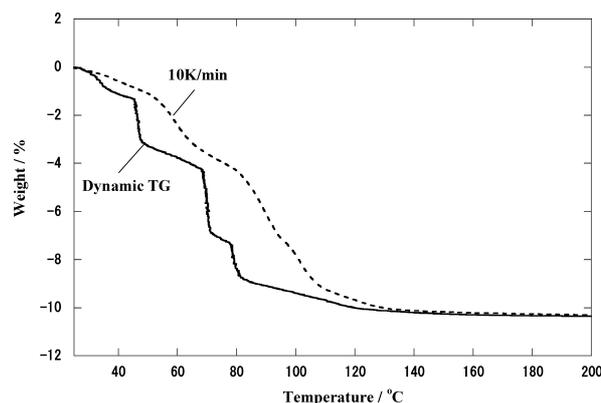


Fig. 2. Comparison data of cyclodextrin obtained by the conventional TG method with constant heating rate of $10^\circ\text{C}/\text{min}$ and the Dynamic TG (CRC mode) method.

accurately. On the other hand, all the reactions are clearly separated in the Dynamic TG curve. The progress of the reactions at constant temperatures of 50 , 70 and 80°C as well as another broad reaction at the temperature range between 80 and 140°C can be clearly observed in the Dynamic TG curve.

The significant differences in reaction temperatures can also be seen in Fig. 2. In the constant heating rate, heating occurs even during a reaction causing the reaction temperature to shift to high temperature. On the contrary, in the Dynamic TG, the reaction temperature is accurately observed because excessive heating does not occur during the progress of a reaction. These results indicate that the resolution of the constant heating method is significantly lower than that of the Dynamic TG curve.

4.2. Changes in thermal behavior

In the conventional thermal analysis, the temperature is controlled as a function of time only, regardless of other possible parameter changes in the sample. Therefore, the temperature is changing during a reaction in the conventional thermal analysis. Also before a reaction ends, depending on the heating rate and the sample amount, the next reaction temperature may be reached, which will result to a different thermal behavior. Since the rate of the evolved gases from the sample can also increase with heating, this may lead to an increase in the concentration of self-generating atmosphere. In some cases, this can also affect the measurement results.

The Dynamic TG (CRC mode) measurement result of zinc acetate dihydrate are shown in Fig. 3, and the three conventional TG curves obtained at three different constant heating rates of 2 , 5 and $20^\circ\text{C}/\text{min}$ as well as the Dynamic TG curve for zinc acetate dihydrate are shown in Fig. 4. A single-step weight loss of 16% can be seen at temperatures below 100°C for each of the four TG curves due to the dehydration of the dihydrate. Each of the three constant heating-rate curves also shows a two-stage weight loss which started at 200°C , while the Dynamic TG curve shows only a single-step weight loss at 200°C (also see Fig. 3). In the constant heating rate,

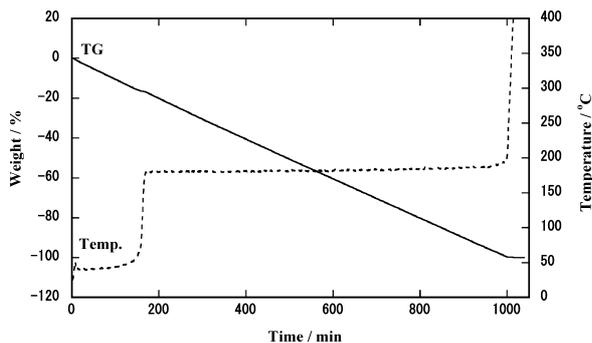


Fig. 3. Dynamic TG (CRC mode) data of zinc acetate dihydrate obtained with a 10-mg sample and a 0.06%/min mass-loss rate.

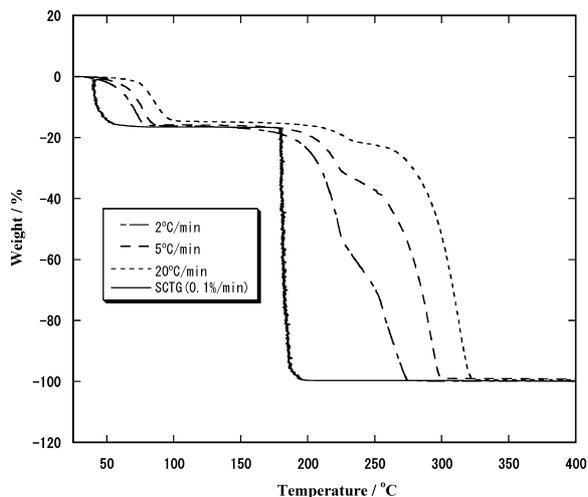


Fig. 4. Zinc acetate dihydrate comparison data of Dynamic TG (CRC mode, SCTG) and constant heating rates of 2, 5 and 20°C/min.

the reaction shifts to low temperature with a slower heating rate, the two mass loss ratios will show a different trend depending on the heating condition. If the heating rate is slow, because the temperature increase during the progress of the reaction will be slightly suppressed, the first level of the reaction amount will be large; if the heating rate is fast during the first level of the reaction, the next reaction temperature will be reached immediately and the second level of the reaction amount will be large.

The Dynamic TG curves plotted in Figs. 3 and 4 show the temperature for the weight loss caused by the second reaction which started at 200°C, while the temperature and the mass-loss rate are unchanged. In other words, an increase in temperature in the sample does not occur until to the end of the first reaction, allowing for the completion of the first reaction. In addition, it is understood that the second reaction was a zero-order reaction that proceeded at the constant temperature, and that sublimation occurred in zinc acetate anhydrate. In the constant heating-rate conditions, oligomerization occurred during sublimation and basic zinc acetate was formed. Also, because the generation of acetone and carbon dioxide were detected at 300°C by a TG-MS

analysis, it is possible that the reaction found at high temperatures was degradation.

4.3. Simulation as an application

Based on our experience, the calcination program of a ceramic part is set depending on a single or multi-step temperature program. When setting the calcination program, it is necessary to consider both the debinding and the sintering processes. Dynamic TG can be used effectively on the temperature simulation of the debinding process. In the debinding process, the temperature increases due to a sudden evolution of gases, which may cause crack formation or changes in form (swell or tear). For this reason, it is necessary that calcination process is done gradually. Excluding the temperature, it is desirable that temperature will change quickly. In order that the binder will be degraded and eliminated at a constant reaction rate in a Dynamic TG analysis, sudden reactions can be suppressed while debinding is carried out. In this case, the obtained temperature curve is the temperature program in the debinding process.

Figure 5 shows the results of a non-sintered alumina material added with an organic binder in the binder extraction process measured at a constant heating-rate of 10°C/min. In the constant heating-rate curves shown in Fig. 5, a two-stage weight loss associated with exothermic peaks by combustion was detected between 150 to 400°C. From this result, in the manufacturing process, when setting the debinding condition in temperatures where combustion occurs, it can be estimated that it will be calcinated from 150°C to 400°C slowly, but the knowledge on the specific temperature program cannot be obtained. On the contrary, temperature control is carried out so that the reaction progresses at a constant mass-change rate in the Dynamic TG measurement. Figure 6 shows the results of the Dynamic TG (CRC mode) measurement obtained from the same non-sintered alumina sample. Sudden reactions, due to debinding, are suppressed; particularly the noticeable exothermic peak associated with combustion is not confirmed in the DTA curve on the second stage of the reaction. In this manner, the temperature curve obtained by Dynamic TG can reflect the effective sintering condition in a real manufacturing

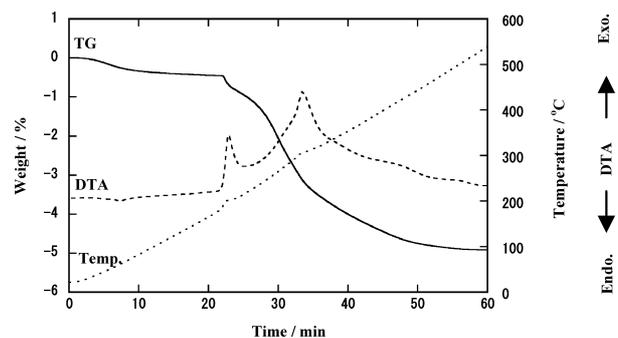


Fig. 5. Debinding process of a non-sintered alumina compact using constant heating rate of 10°C/min.

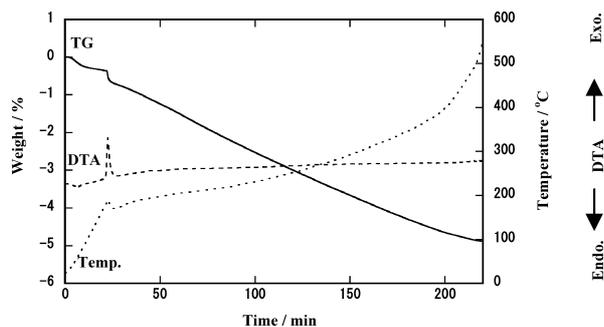


Fig. 6. Debinding process of a non-sintered alumina compact using Dynamic TG (CRC).

process.

5. Dynamic TMA

Dynamic TMA is a temperature control technique with the contraction rate as a control parameter. The technique is commonly used in the sintering process of ceramic materials. The calcination conditions of ceramic materials are divided into debinding process and sintering process, as mentioned in Section 4.3. Dynamic TMA is used for the simulation of the temperature condition during the sintering process and the formation of sintered materials using different sintering rates. The contraction rate of ceramics is affected by the grain growth during sintering. Therefore, it is possible that the difference in the contraction rate in the sintered materials give rise to the difference in their physical properties. Figure 7 shows the Dynamic TMA measurement results of a non-sintered alumina material. Sintering associated with contraction began to occur from 1000°C, and the temperature control was carried out to keep a constant contraction rate. The temperature curve also shows the temperature condition in which sintering was performed.

In a Dynamic TMA measurement, it is possible to control the contraction rate when a ceramic material is being sintered. Contractions by different random contraction rates can develop new sintered ceramic materials. Using the Dynamic TMA in performing an experiment and in evaluating the physical properties of a ceramic material, the contraction rate to obtain the most suitable physical properties can be studied. Figure 8

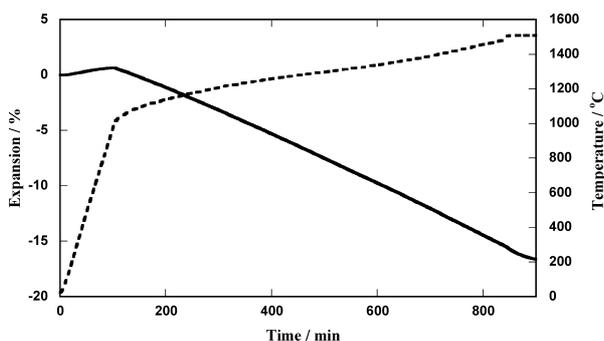


Fig. 7. Sintering process of a non-sintered alumina compact using Dynamic TMA (CRC mode, 0.02%/min).

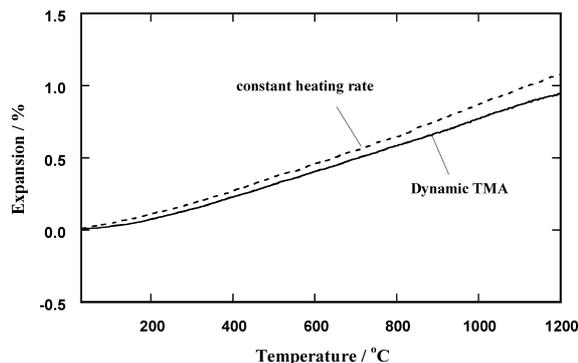


Fig. 8. A comparison of the thermal expansions in the sintered alumina material obtained by the constant heating-rate and Dynamic TMA sintering methods.

shows a comparison of the thermal expansions in the sintering of a sintered alumina material by the constant heating rate of 10°C/min and by the Dynamic TMA method using a 0.02%/min contraction rate. The results show that the sintered alumina material, which is gradually sintered using the constant contraction rate in a Dynamic TMA measurement, had a lower expansion. It is presumed that the effective densification of the grains was due to the gradual sintering at a constant reaction rate.

6. Conclusion

When studying the reaction mechanism in a controlled-rate thermal analysis, it is important that the reaction rate is kept constant during a measurement. The examples presented in this article show that the constant reaction control (CRC) mode is best suited for such an analysis. It is also important to ensure first that the mass-change curve changes linearly. If the curve is nonlinear, a detailed analysis of the reaction mechanism will be difficult.

The controlled-rate thermal analysis measures using a different temperature control than the conventional thermal analysis, namely the constant heating-rate method. Therefore, these two methods are basically different. In some cases, the results of the controlled-rate thermal analysis give the same results as those obtained by the constant heating-rate analysis, but not in most cases. In order to accurately judge a thermophysical property, it is necessary to take note of the influence of self-cooling and self-heating effects, because the reaction rate changes in the constant heating-rate method. The changes in self-generated atmosphere should also be taken into consideration. On the contrary, the controlled-rate thermal analysis strictly controls the self-generated reaction condition more than the conventional thermal analysis (the partial pressure of the evolved gas in the reaction system is kept constant). In the controlled-rate thermal analysis, the temperature changes caused by reactions within a sample, such as self-cooling due to endothermic or self-heating effect caused by exothermic, can also be suppressed. For this reason, the controlled-rate thermal analysis can

effectively observe an essential reaction in a sample. As described in the simulation as an application, an effective knowledge can also be obtained.

References

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