Technical know-how in thermal analysis measurement —Thermal analysis under water vapor atmosphere—

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1. Introduction

In thermal analysis, the measurement condition influences the measurement results. Therefore, it is important to select the most desirable measurement condition in response to the objective of the measurement.

Conditions such as sample amount, heating rate as well as the measurement atmosphere are selected freely in thermal analysis measurement. Especially the measurement atmosphere, where it directly affects the sample's reaction, for example, measuring under atmospheric air may cause combustion or oxidation reaction and the suppression of these reactions can be confirmed by measuring under inert atmosphere. Therefore, it is essential to select the appropriate atmospheric gas suitable to the objective of the measurement.

But the difference among atmospheric gases is not only the presence or absence of oxygen (O_2), such as when using an air pump for an air atmospheric measurement also includes the room humidity (water vapor partial pressure) while using a gas cylinder for an inert gas atmospheric measurement creates a dry atmosphere(1).

The dehydration behavior of the sample is most affected by the effects of humidity and in some cases degradation reaction may also be affected. Hence, it is important to measure under a predetermined humidity to perform simulation on the sample's thermal behavior. Also, evaluating the material's hygroscopic behavior (percentage of water absorption) as a property is the most important factor. On the other hand, since dehydration behavior is determined from the heating process, accurately estimating the coefficient of water absorption is extremely difficult in the conventional thermal analysis.

In recent years, various fields of specialization have applied thermal measurements where humidity in the atmosphere is controlled because of its ease and simplicity. Although the effects of humidity on the measurement results were thoroughly discussed in 2009(1), this paper discusses the basic terminologies related to humidity, thermal analysis under water vapor atmosphere and its measurement methods. It also includes applications such as effects of water vapor on the thermal degradation of polymers and organic metal compounds; and measurement of adsorption and desorption of moisture levels in relation to change in humidity. Finally, this paper ends with a general conclusion.

2. Definition of humidity

Humidity is defined as the amount of water vapor (H_2O gas) in gas (atmosphere), where values are expressed in several units. Most familiar and deeper terminology is the relative humidity, expressed in percentage, which refers to the ratio of the amount of water vapor at a particular temperature to the amount of saturated water vapor (also used in weather forecasts). Shown below are related terminologies of humidity and their units of expression.

- ◆ Water vapor partial pressure (vapor pressure), Pa, is the partial pressure of water vapor in gas
- ◆ Relative Humidity, % RH, is the ratio of the partial pressure of water vapor at a particular temperature to the saturated water vapor pressure expressed in percentage.
- ◆ Absolute humidity, kg/m^3 is the mass of water vapor per unit volume ($1\ m^3$).
- ◆ Dew point temperature, °C, is the temperature at which the water vapor pressure is equivalent to the saturated water vapor.

3. Thermal analysis under water vapor atmosphere

3.1. Modular structure

When performing a thermal analysis measurement under a water vapor atmosphere, the modular structure consists of (1) a humidity generator allowing the generation of an arbitrary water vapor concentration (humidity generator, HUM-1 by Rigaku), (2) an isothermal-type thermal analysis module without the occurrence of condensation even under high humidity concentration; and (3) a circulator for an isothermal-type thermal analysis module. Also, when conducting a measurement under a humid atmosphere (25°C, 90%RH) without condensation, measurement can be done using a standard thermal analyzer attached with a water vapor generator.

3.2. Measurement range

Generally, the thermal analysis module equipped with

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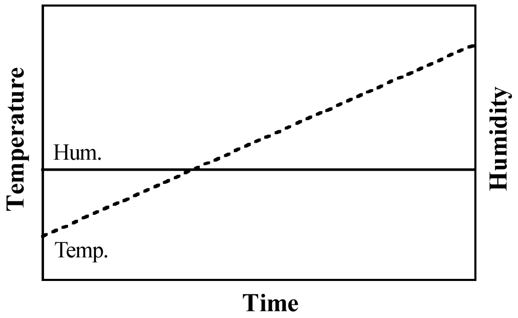

Fig. 1. Constant water vapor partial pressure at a constantly changing temperature.

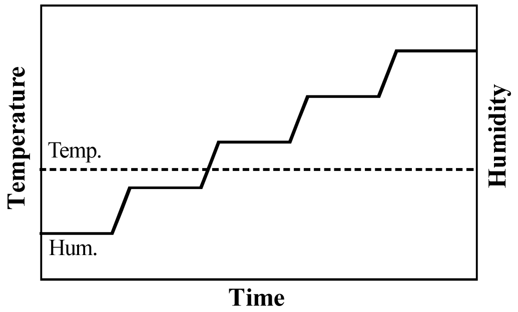

Fig. 2. Constant temperature at a stepwise change in water vapor partial pressure.

isothermal furnace used for water vapor atmosphere has a similar specification with the standard thermal analysis module where it can be heated up to a maximum of 1500°C, to avoid water condensation. Also, it can be humidified up to a maximum water vapor concentration of 80°C, 90% RH.

4. Thermal analysis measurement technique under humidity controlled atmosphere

Humidity controlled thermal analysis is categorized into 2 major types namely, a measurement where the water vapor concentration is held constant at a changing temperature; and a measurement where changes in water vapor concentration is performed at an isothermal condition.

4.1. Measurement at a constant humidity

The conventional thermal analysis technique pays less attention on the humidity condition. Therefore, performing a thermal analysis measurement under an arbitrary humidity as a measurement atmosphere condition enables to compare the material's thermal behaviors in response to different humidity conditions. Fig. 1 illustrates a thermal analysis measurement condition showing a constant water vapor partial pressure at a constantly changing temperature.

4.2. Constant temperature measurement at a changing humidity

Changing the humidity at an arbitrary isothermal temperature condition is a technique where the amount of water absorbed or desorbed from the sample is measured. Figure 2 illustrates a thermal analysis measurement condition showing a constant temperature at a stepwise change in water vapor partial pressure. Plotting humidity against the amount of change will represent the adsorption isotherm.

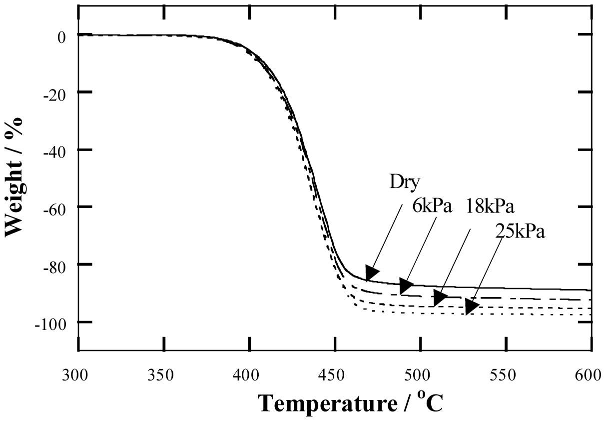

Fig. 3. TG results with different levels of water vapor partial pressure.

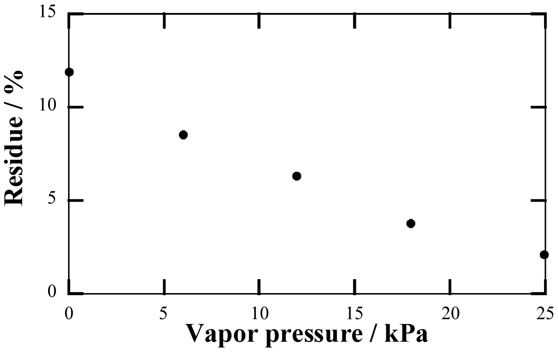

Fig. 4. Residual ratio at 500°C.

5. Effect of water vapor on the thermal degradation reaction

5.1. Thermal degradation of resin(2)

Figure 3 shows the TG result of PET in N_2 atmosphere with different water vapor partial pressure. Although mass losses due to degradation is seen from 350°C to 450°C, the reaction occurred at low temperature for measurements with high water vapor partial pressure and the mass loss ratio tends to be large. Figure 4 shows the plotted result of the residual amounts at 500°C with regards to the respective water vapor partial pressure.

It is understood that increasing the water vapor partial pressure is associated with a decrease in residual amount. Although carbon still remains after thermal degradation of PET (polyethylene terephthalate) under inert dry atmosphere, it suggests that as water vapor partial pressure increases, the thermal degradation reaction controlling the carbonization phenomena occurs. Usually, it is known that PET is degraded into ethylene glycol and terephthalic acid during hydrolysis. A similar measurement was performed using water vapor TG-MS (thermogravimetry coupled with mass spectrometry) and the generation of ethylene glycol and terephthalic acid were confirmed. Under humidity controlled atmosphere, the degradation of PET as well as hydrolysis simultaneously occurred, thus the higher the water vapor partial pressure, the lesser the carbon residue.

5.2. Thermal behavior of organic metal compounds

Figures 5 and 6 show the respective TG curve and DTA curve of zinc acetylacetonate monohydrate ($C_{10}H_{14}Zn \cdot H_2O$) measured under different levels of water vapor partial pressure. Under dry atmosphere, the TG curve showed more than 90% mass losses while the DTA curve showed 4 endothermic peaks. Associated with an increase in water vapor in the TG curve are mass losses in the TG shifting to low temperature with a tendency of a smaller mass loss ratio. While the first and fourth peaks in the DTA curve tend to shift towards the high temperature and low temperature, respectively. Furthermore, the water vapor partial pressure at 9.3 kPa condition showed that the residual amount agrees to the theoretical generation of zinc oxide, the DTA curve is reduced to 2 endothermic peaks. On the other hand, the results of TG-MS and XRD-DSC (simultaneous measurement of XRD and DSC) indicated that the thermal behaviors of zinc acetylacetonate monohydrate are in the following order: dehydration, transition, melting and evaporation. All these associated endothermic reactions are confirmed in the DTA curve. The increase in water vapor partial pressure associated with dehydration inhibited the reaction resulting to a shift towards high temperature. This result indicated that the degradation of the hydrate state progressed.

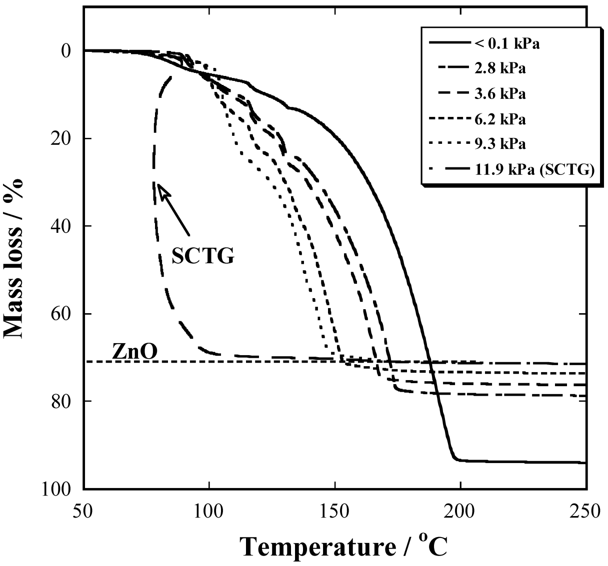

Fig. 5. TG results of $C_{10}H_{14}Zn \cdot H_2O$ under different levels of water vapor atmosphere.

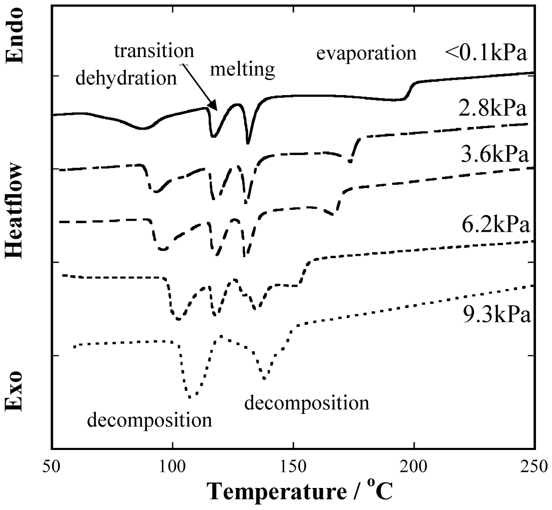

Fig. 6. DTA results of $C_{10}H_{14}Zn \cdot H_2O$ under different levels of water vapor atmosphere.

As a result, only degradation of the hydrate occurred when measured under high water vapor atmosphere condition and that the reaction progressed into 2 stages. In addition, although the DTA curve showed that the increase in water vapor partial pressure to $P_{H_2O}=6$ kPa did not affect the transition and melting as shown in the DTA curve, but as the vapor pressure increased to $P_{H_2O}=9.3$ kPa, the degradation caused chemical changes in the sample and peaks due to transition and melting disappeared. Also, accelerating the degradation reaction associated with an increase in water vapor partial pressure allowed the evaporation reaction to complete in the low temperature shifting the peak due to evaporation towards the low temperature.

In the humidity controlled atmosphere of Dynamic TG (sample controlled thermogravimetry: SCTG), the degradation progressed below 100°C and that ZnO was confirmed as a residue. From this measurement result, performing thermal treatment under humidity controlled atmosphere below 100°C enabled the direct generation of ZnO from zinc acetylacetonate monohydrate.

6. Measurement of adsorption and desorption of moisture levels due to change in humidity

The sample is held at isothermal and stepwisely changing the humidity enables to measure the amount of moisture absorbed and desorbed with regards to humidity. Figure 7 shows the TG result of perflouro-

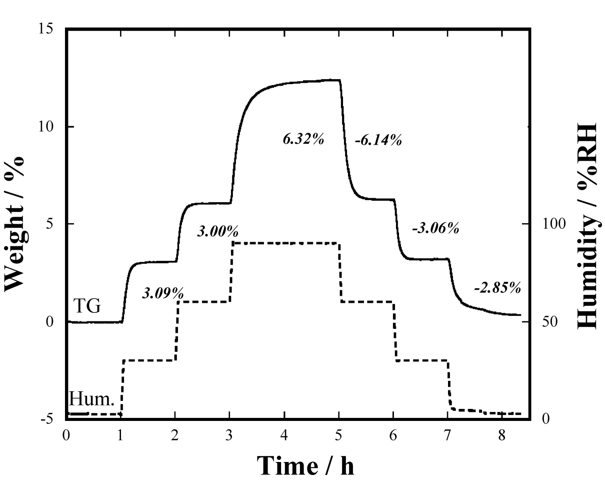

Fig. 7. TG result of perflourosulfonic acid.

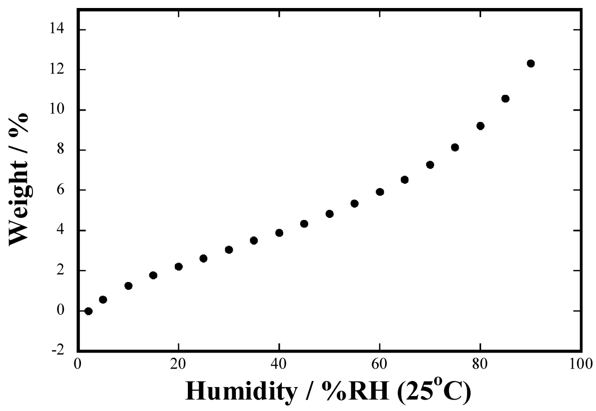

Fig. 8. Absorption isotherm of perflourosulfonic acid membrane.

sulfonic acid membrane isothermally held at 25°C while humidity was changed stepwisely from dry→30%RH→60→90→60→30→dry. In the TG results, an increase in mass was seen due to an increase in humidity associated with absorbed moisture and a decrease in mass was confirmed due to a decrease in humidity accompanied with dehydration.

Similarly, a measurement with more detailed changes in humidity was performed and the absorbed water ratio in relation to relative humidity is plotted in Fig. 8.

In less than 10%RH, the water adsorption ratio of persulfonic acid membrane is high in the low humidity condition and then at 60%RH, the water adsorption increased almost linearly. The water adsorption ratio in relation to change in humidity further increased at a high relative humidity condition of 60%RH. This indicates that the water adsorption property of the sample in response to various humidity levels is different. The graph showing the gaseous concentration (partial pressure) plotted against amount absorbed is called an adsorption isotherm, where the adsorption mechanism of the curve depends on the surface profile and pore size of the sample.

Figure 9 shows the TG result of the inclusion organic compound in cyclodextrin measured under controlled humidity which was carried out at room temperature (25°C) from dry→90%RH→dry condition and then heated at dry condition. Due to change in humidity at room temperature, a 6.5% adsorption–desorption reaction was confirmed. On the other hand, 5.5% dehydration was confirmed in the heating process indicating that the difference in dehydration behavior was due to difference in water binding energy. Identifying adhesive water (free water) as well as bound water (crystal water) in materials such as organic compounds and pharmaceuticals is extremely important; it is usually differentiated thru their dehydration temperature using the constant heating method in the TG. However if the dehydration temperature of the bound water is near the room temperature, identification will be complicated. As shown earlier, water is differentiated as adhesive water and free water where the former is the type of water which reacts to change in humidity while the latter is the type of water which does not react to change in humidity. As shown earlier, loosely bound water or free water may or may not react on change humidity.

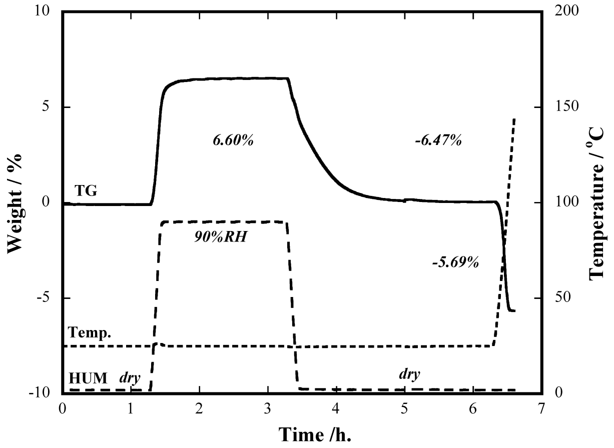

Fig. 9. TG result of cyclodextrin.

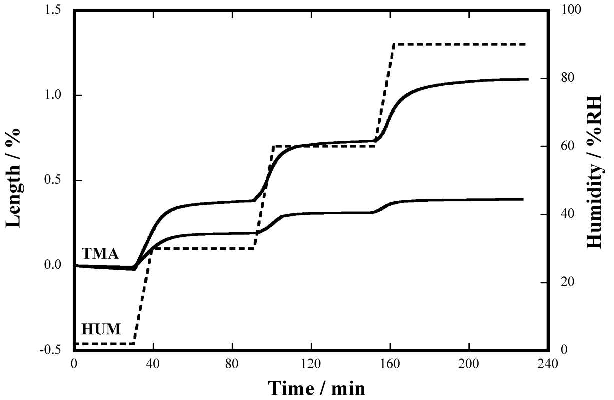

Fig. 10. TMA results of a photocopy paper and a coat paper.

7. Change in dimension due to change in humidity

We have discussed the evaluation of adsorbed water ratio (adsorption-desorption associated with mass change) using TG in Section 6. The amount of swelling with regards to change in humidity can be measured using TMA. Figure 10 shows the moisture adsorption property measurement results of a photocopy paper and a coat paper at room temperature using TMA. The sample's expansion was measured at room temperature (25°C) while the atmosphere's humidity was changed from dry→25°C30%RH→60%RH→90%RH. Although expansion associated with increase in humidity were observed in both paper samples but differed in the amount of expansion. Comparing the 90% RH and the dry atmosphere, the respective expansions were 1.1% in photocopy paper and 0.4% in coat paper indicating that the effect of humidity in the change in dimension of the coat paper was small.

8. Conclusion

This article has introduced the use of humidity or a humidity generator to perform thermal analysis under controlled humidity. When compared to the conventional thermal analysis where it neglects the humidity, the application of humidity as a measurement condition broadens the measurement condition which may lead to obtaining new information of the material.

Humidity related thermo-physical properties such as dehydration reaction, hydrolysis, glass transition, sintering are affected by humidity, also hydrates such as the zinc acetylacetonate monohydrate where the reaction is likely to change. In addition, it is possible to evaluate properties such as amount adsorbed or swelling amount to obtain a clear and detailed knowledge in relation to moisture adsorption property which cannot be accomplished in the conventional thermal analysis. Also, when performing material evaluation, it is usually summarized as "evaluating at nearly the same atmosphere of the usage environment."

Although thermal analysis is considered as one of the simple measurement techniques that can be performed in such evaluation, "humidity" always exists in atmospheric environments and cannot be neglected. In addition "humidity" varies according to place, time and season.

Performing thermal analysis under a controlled humidity atmosphere is a promising tool where the humidity can be arbitrarily changed because it enables evaluation at the same atmosphere as the usage environment, hoping to solve problems or screen materials effectively.

References

(1) Y. Masuda and L. Celiz: *The Rigaku Journal (English version)*, **25** (2009), No. 1, 15–18.

(2) T. Arii and Y. Masuda: *J. Anal. Appl. Pyrolysis*, **71** (2004), 525–536.