

Application News

No. T160

Thermal Analysis

Characterization of Polyethylene Materials by Thermal Analysis

Polyethylene (PE) is the most widely used polymer material, with applications including films, general molded products, electrical insulation, ropes, hoses, and others.

PE is classified by density and production method as low density polyethylene (LDPE), medium density polyethylene (MDPE), or high density polyethylene (HDPE). Numerous types such as linear low density polyethylene (LLDPE) and ultra-high molecular weight polyethylene (UHMW-PE) also exist, depending on the structure and molecular weight of the PE.

These various types of polyethylene have different properties, including crystallinity, melting temperature, and decomposition temperature, and are used corresponding to the application of the product.

This article introduces examples in which the thermal properties of several types of polyethylene were evaluated using the thermal analysis techniques DSC, DTG (TG-DTA), and TMA, and describes the usefulness of those techniques.

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■ Measurement of Plastic Transition Temperature (DSC)

The melting point and crystallization temperature of polyethylene can be measured with a differential scanning calorimeter (DSC). The melting point is represented by the melting peak temperature in the DSC curve and can be used in qualitative analysis. It is also an indicator of the lowest temperature during molding processing.

Fig. 1 shows the results of a measurement of the transition temperature of a plastic as provided in JIS K 7121-2012 using LDPE as the sample material. During heating, the endothermic peak of melting is detected at around 112 °C, and during cooling, the exothermic peak of crystallization is detected at around 99 °C. Table 1 shows the measurement conditions in this experiment.

Table 1 Measurement Conditions

Temperature range	: 25 °C → 170 °C → 25 °C → 170 °C (holding for 10 min at 170 °C)
Heating Rate / Cooling Rate	: 10 °C/min
Sample weight	: 5 mg (approx.)
Cell	: Aluminum crimp cell
Atmosphere	: N ₂

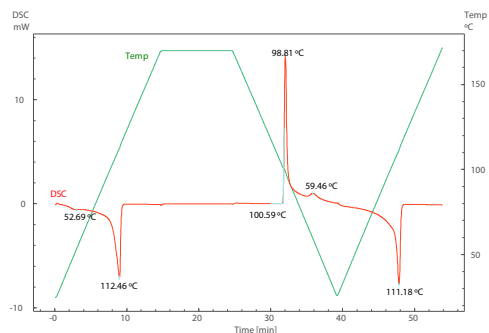


Fig. 1 Measurement of Transition Temperature of LDPE

■ Measurement of Melting and Crystallinity (DSC)

The hardness, impact resistance, transparency, and other physical properties of polymer materials change depending on the degree of crystallinity. For example, although materials become harder as crystallinity increases, they also become brittle and less impact-resistant. The degree of crystallinity can be calculated by the following equation using the melting peak area (heat of fusion) measured by DSC.

$$\text{Crystallinity (\%)} = (\text{Measured heat of fusion} / \text{Heat of fusion for perfect crystal}) \times 100$$

Fig. 2 shows an example in which three types of polyethylene (LDPE, HDPE, UHMW-PE) were measured and their crystallinities were obtained. Here, 290 J/g was used as the heat of fusion for a perfect crystal.

From these data, it can be understood that crystallinity increases and the melting peak temperature shifts to higher temperatures as the density of the polyethylene becomes greater.

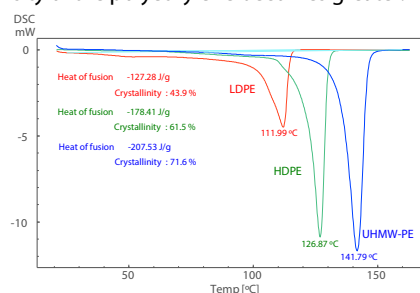


Fig. 2 Measurement of Crystallinities of Various Types of Polyethylene

■ Thermal Decomposition Characteristics – Differences due to Density (TG-DTA)

It is possible to evaluate the heat resistance of materials by measuring the process of thermal decomposition.

Fig.3 shows the results of a measurement of the thermal decomposition characteristics of LDPE and HDPE with a Shimadzu DTG-60 (simultaneous thermogravimetry/differential thermal analysis (TG-DTA)) in a nitrogen atmosphere.

These data show that decomposition begins at a lower temperature in LDPE than in HDPE, indicating that LDPE has lower heat resistance. As the reason for this difference, it is estimated that decomposition of LDPE proceeds more easily due to the relatively large number of branches in its molecular structure.

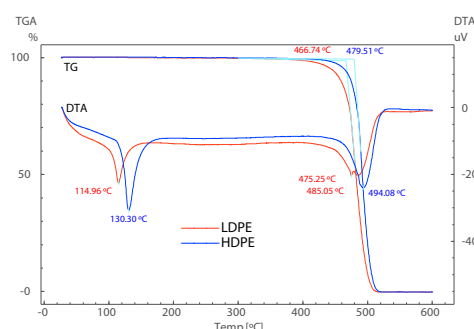


Fig. 3 Thermal Decomposition of LDPE and HDPE (Atmosphere: N₂)

Thermal Decomposition Characteristics – Differences due to Atmosphere (TG-DTA)

Fig. 4 shows the results of a measurement of HDPE with the DTG-60 under two types of atmospheres, nitrogen and air. In a nitrogen atmosphere, TG-DTA measures the process by which the sample decomposes mainly due to heat. In TG, a first-stage mass decrease is detected in the vicinity of 500 °C, and an endothermic peak is also detected by DTA. In air, TG-DTA measures the process of material decomposition mainly by the reaction with oxygen (i.e., combustion). The TG analysis confirmed mass loss in multiple stages from a relatively low temperature region, while DTA detected multiple exothermic peaks. Under both atmospheres, the endothermic peak at 130 °C in the DTA corresponds to melting. These data demonstrate the importance of selecting an appropriate atmosphere gas corresponding to the purpose when evaluating the thermal decomposition (heat resistance) of polymer materials.

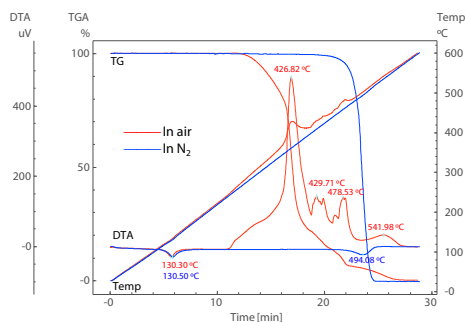


Fig. 4 Difference of Thermal Decomposition of HDPE by Atmosphere

Thermal Decomposition Characteristics – Differences due to Heating Rate (TG-DTA)

Although an index of the decomposition temperature of polymer materials can be obtained by DTG, care is necessary, as the obtained index is a relative value under the measurement conditions used in the test. In particular, if measurements are conducted under different heating rates, the decomposition temperature will change depending on the rate.

Fig. 5 shows the results of a DTG measurement when the heating rate was changed in the range of 5 °C/min to 20 °C/min. As the heating rate becomes faster, both the TG curve and the DTA curve shift to the high temperature side. Comparing the temperatures at which 10 % mass loss occurs in the TG curve, differences can be seen between 430 °C and 460 °C. Thus, it is necessary to use a constant heating rate when evaluating the decomposition process by DTG.

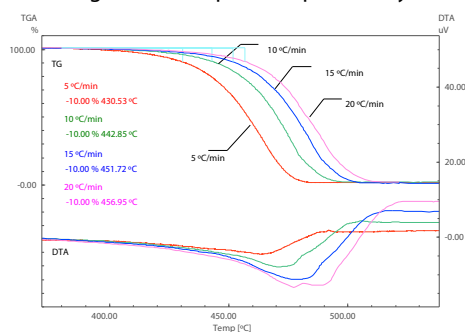


Fig. 5 Difference of Decomposition Temperature of LDPE by Heating Rate

Measurement of Thermal Deformation Temperature (TMA)

Thermomechanical analysis (TMA) is effective in evaluations of the thermal deformation temperature of polymer materials. In TMA, one of the following modes is generally selected, depending on the sample shape and the purpose of the evaluation.

- ① Expansion
- ② Penetration
- ③ Elongation

Here, the thermal deformation temperature (softening point) was measured and introduced using penetration mode.

Fig. 6 shows the measurement set-up. The process in which the tip of the penetration probe placed on the sample passes through the sample accompanying sample softening under heating is measured.

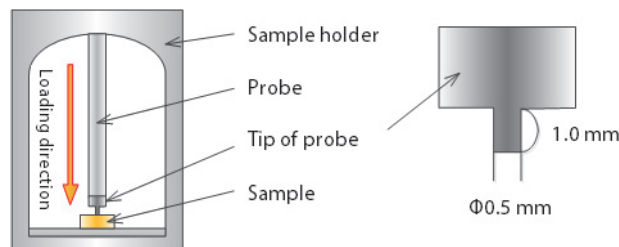


Fig. 6 Measurement of Thermal Deformation Temperature (Softening Point) by TMA

Fig. 7 shows the results of a measurement of LDPE and HDPE. Here, the samples were heated while applying a load of 50 g. From these data, it can be understood that softening and deformation occur at a lower temperature in LDPE.

Thus, it is possible to evaluate the thermal deformation temperature (softening point) of polymer materials by TMA measurement in the penetration mode.

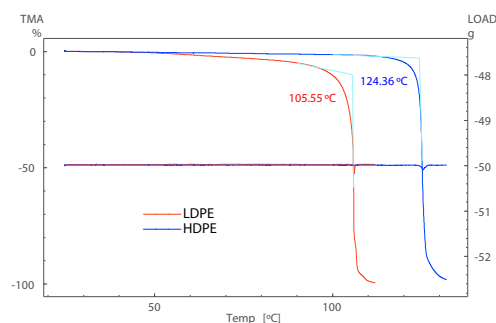


Fig. 7 Difference of Softening Points of LDPE and HDPE

Conclusion

In these experiments, the changes which occur in polyethylene, a representative polymer material, under heating were evaluated from multiple perspectives using various thermal analysis methods. Clear differences in the thermal properties of several types of polyethylene were observed, depending on differences in the degree of crystallinity (density).

Because differences in the crystal structure are reflected in the thermal property data, thermal analysis is considered to be an evaluation technique with wide applicability to characterization of other general polymer materials.