Application Brief

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Evaluation of Crystallinity for Crystalline Polymers

Melting measurement by DSC and Equilibrium melting enthalpy

1. Introduction

Typical crystalline polymers, such as polyethylene (PE), polypropylene (PP), polyamide (PA), and polyethylene terephthalate (PET), have a mixture of crystal, in which the molecular chains are regularly arranged, and amorphous, which exist in a randomly entangled state. The ratio of crystalline to amorphous varies depending on the type of polymer and also on the thermal history of the same polymer. The degree of crystallinity is an important higher-order structural factor that determines the mechanical strength, thermal properties, and other properties of various materials such as fibers, films, and injection molded products. Various methods are used to evaluate crystallinity, such as density method, wide-angle X-ray diffraction, FT-IR, solid-state NMR, and thermal analysis.

In the evaluation of crystallinity by thermal analysis, the data of melting from DSC measurement is used. Figure 1 shows an image of melting and crystallization as observed by DSC. In DSC measurements of melting phenomena, the process of crystal collapse and randomization is observed. Therefore, the size of the melting peak measured by DSC is proportional to the amount of the crystal. The ratio of the melting enthalpy, ΔH_m, obtained from the area of the melting peak to the equilibrium melting enthalpy, ΔH_m^0, which corresponds to the melting enthalpy of 100 % crystalline polymer, can be used to determine the ratio of the crystal to the total, crystallinity, χ_c.

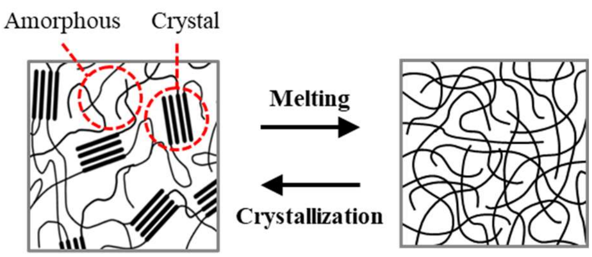

Figure 1 Image of melting and crystallization for crystalline polymer

This report introduce an example of determining the degree of crystallinity of polyethylene (PE), polyamide (PA), and polyethylene terephthalate (PET) using the equilibrium melting enthalpies of the respective polymers from DSC melting measurements.

2. Calculation of Crystallinity

From the melting enthalpy obtained by the DSC measurement, the degree of crystallinity can be calculated using the following equation[1)].

$$\chi_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \quad \cdots\cdots (1)$$

ΔH_m is the actual melting enthalpy measured by DSC, and ΔH_m^0 is the equilibrium melting enthalpy corresponding to the melting enthalpy of 100 % crystalline polymer. In DSC, the sample is specified in terms of mass, g, so the crystallinity χ_c obtained by the equation (1) is the mass fractional crystallinity.

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In the case of crystalline polymers that occurs cold crystallization during the heating process, the degree of crystallinity can be determined from the ratio of the equilibrium melting enthalpy ΔH_m^0 to the difference between the cold crystallization enthalpy ΔH_c and the melting enthalpy ΔH_m, as shown in the following equation.

$$\chi_c(\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \times 100 \quad \cdots\cdots (2)$$

3. Calculation of crystallinity for polyethylene

Figure 2 shows the DSC measurement results for low-density polyethylene, LDPE, and high-density polyethylene, HDPE[2]. These are the measurement results for two types of LDPE and three types of HDPE with different densities. In these results, the higher the density, the higher the melting temperature and the larger the melting enthalpy. Table 1 shows the degree of crystallinity calculated from the equilibrium melting enthalpy[1] of polyethylene based on the measurement results in Figure 2.

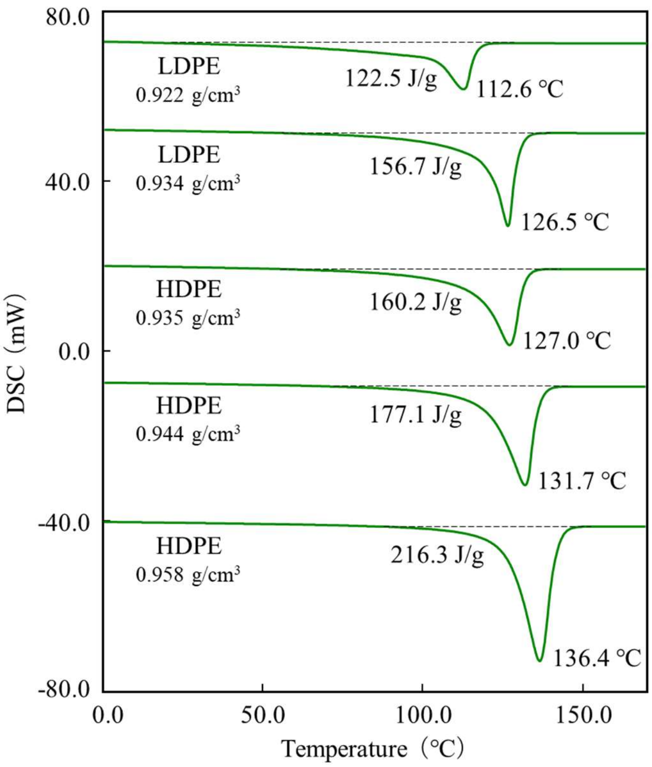

Figure 2 DSC curves for LDPE and HDPE [2]

Table 1 Crystallinity of the polyethylene

Polyethylene	Equilibrium melting enthalpy[1] ΔH_m^0 (kJ/mol)	Dencity (g/cm^3)	Melting enthalpy ΔH_m (J/g)	Crystallinity χ_c (%)
LDPE	4.11	0.922	122.5	41.8
		0.934	156.7	53.5
HDPE		0.935	160.2	54.7
		0.944	177.1	60.5
		0.958	216.3	73.8

4. Calculation of crystallinity for polyamide

Figure 3 shows the DSC measurement results for polyamide 6, N6, and polyamide 66, N66[3]. The glass transition, cold crystallization, and melting of N6 are observed around 35 to 45 °C, 55 to 85 °C, and 190 to 230 °C, respectively. Also, the glass transition, cold crystallization, and melting of N66 are observed around 40 to 45 °C, 50 to 80 °C, and 200 to 270 °C, respectively.

Table 2 shows the crystallinity of the polyamides calculated from the equilibrium melting enthalpies[1] of the polyamides based on the cold crystallization enthalpies and melting enthalpies obtained from the measurement results in Figure 3.

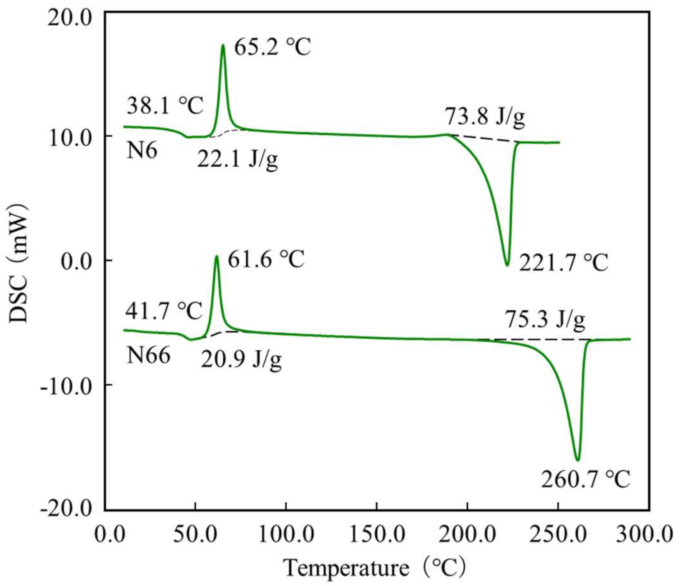

Figure 3 DSC curves for N6 and N66 [3]

Table 2 Crystallinity of the polyamides

Polyamide	Equilibrium melting enthalpy[1] ΔH_m^0 (kJ/mol)	Cold crystallization enthalpy ΔH_c (J/g)	Melting enthalpy ΔH_m (J/g)	Crystallinity χ_c (%)
N6	26.0	22.1	73.8	22.5
N66	57.8	20.9	75.3	21.3

5. Calculation of crystallinity for polyethylene terephthalate

Figure 4 shows the measurement results of the 1st heating of the screw, the center of the bottle and the bottom of the PET bottle[4]. Even though it is a one-piece molded product, the DSC curve differs depending on the part. Like polyamide, PET is a crystalline polymer that occurs cold crystallization during the heating process. In the screw and bottom, the glass transition, cold crystallization, and melting are observed around 70 to 80 °C, 120 to 140 °C, and 220 to 260 °C, for both parts. The glass transition and cold crystallization are observed in both parts, indicating a high amorphous content. On the other hand, in the measurement results at the center of the bottle, the endothermic peak of melting is observed around 220 to 260 °C, but the glass transition and cold crystallization are hardly observed. In the center of the bottle, the glass transition and cold crystallization are not observed, indicating that there are many crystalline parts.

Table 3 shows the crystallinity of polyethylene terephthalate calculated from the equilibrium melting enthalpy[1] of polyethylene terephthalate based on the cold crystallization enthalpy and melting enthalpy obtained from the measurement results in Figure 4.

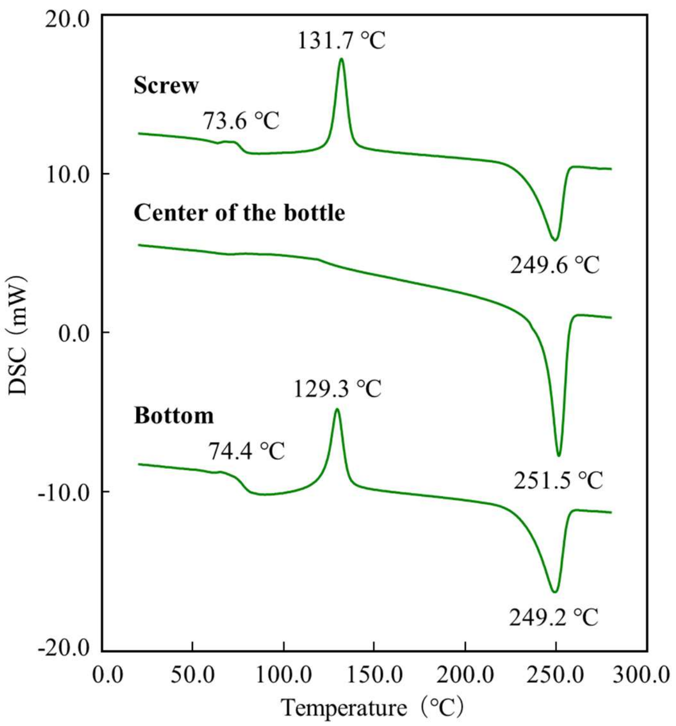

Figure 4 DSC curves for PET bottle (1st heating) [4]

Table 2 Crystallinity of the PET bottle (1st heating)

Part	Equilibrium melting enthalpy[1] ΔH_m^0 (kJ/mol)	Cold crystallization enthalpy ΔH_c (J/g)	Melting enthalpy ΔH_m (J/g)	Crystallinity χ_c (%)
Screw		31.5	43.6	8.6
Center	26.9	0*	63.6	45.4
Bottom		36.1	51.6	11.1

Figure 5 shows the measurement results of the 2nd heating of the screw, the center of the bottle and the bottom of the PET bottle[4]. The results of the 2nd heating show the same DSC curve for each part. Each of these parts was heated in the 1st heating until the melting was completely finished, and then quenched to room temperature, which erased the thermal history of the molding of this PET bottle. And since the same thermal history of quench was given, the same result was obtained for each part.

Table 4 shows the crystallinity of polyethylene terephthalate calculated from the equilibrium melting enthalpy[1] of polyethylene terephthalate based on the cold crystallization enthalpy and melting enthalpy obtained from the measurement results in Figure 5. It can be seen that the degree of crystallinity for each part is similar.

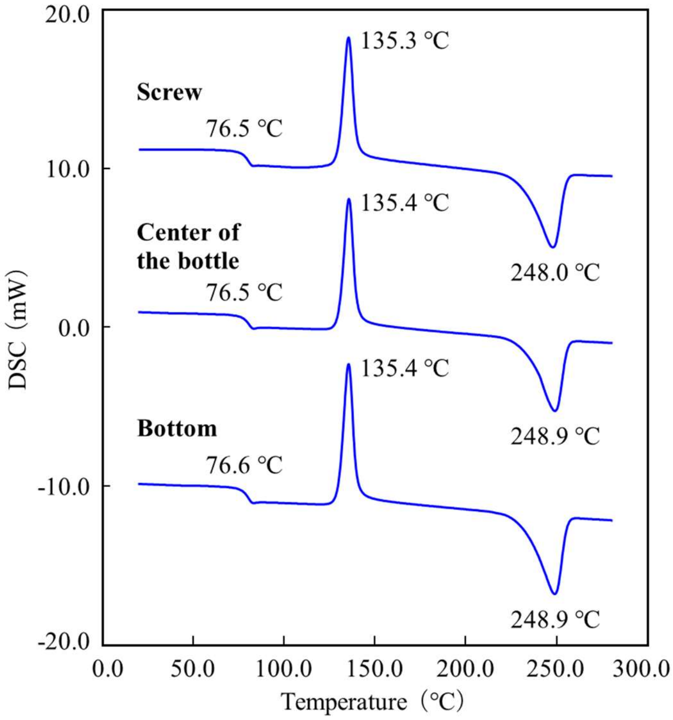

Figure 4 DSC curves for PET bottle (2nd heating)[4]

Table 2 Crystallinity of the PET bottle (2nd heating)

Part	Equilibrium melting enthalpy[1] ΔH_m^0 (kJ/moℓ)	Cold crystallization enthalpy ΔH_c (J/g)	Melting enthalpy ΔH_m (J/g)	Crystallinity χ_c (%)
Screw	26.9	36.7	44.6	5.6
Center		34.4	41.6	5.1
Bottom		37.5	45.1	5.4

Reference

1) B. Wunderlich, Macromolecular Physics, Vol.1, Academic press (1973)
2) Application Brief TA No.26, DSC Measurement of Polyethylene, Hitachi High-Tech Science Corporation (2021)
3) Application Brief TA No.94, DSC Measurement of Polyamide, Hitachi High-Tech Science Corporation (2021)
4) Application Brief TA No.7, Evaluation of Plastic Molding, Hitachi High-Tech Science Corporation (2021)