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Hitachi High-Tech Science Corporation

TA No.7

2021.4

Evaluation of Plastic Molding

DSC Measurements for PET Molding Products

1. Introduction

Plastics can be made to have a variety of properties depending on the molding method. In general, for molded products such as containers that require dimensional stability, it is desirable for the material structure to be amorphous. In addition, in films and fibers, molecular orientation is used to increase strength in a directional property. By investigating differences in properties such as crystallinity and molecular orientation using DSC, it is possible to evaluate the molding methods and processing conditions of various plastics.

In this report, we introduce an example of DSC evaluation of the difference in properties of extruded PET sheet, stretched PET film, and blow molded PET bottle as molded polyethylene terephthalate, PET, products with different molding methods.

2. Measurements

The samples were extruded PET sheet with a thickness of 500 µm, stretched PET film with a thickness of 100 µm, and commercially available PET bottle for beverages. The PET bottle was measured at three sampling points: the screw, the center of the bottle, and the bottom.

For DSC, the NEXTA DSC600 High Sensitivity Differential Scanning Calorimeter was used. For the measurement conditions, the sample mass was about 10 mg, and the temperature range was 20 to 280 °C with a heating rate of 10 °C/min. Each sample was heated up to 280 °C for the first time, quenched to room temperature after the sample was completely melted, and then heated up for the second time under the same measurement conditions.

3. Extrusion molding, Stretching and Blow molding

In extrusion molding, molten thermoplastic resin is extruded through an extrusion port, die, with a hole of a specific shape, and then cooled to produce a molded product of a certain shape. It is widely used in the manufacture of molded products with the same cross-sectional shape and length, such as seats, tubes, and pipes.

Stretching is the process of drawing a sheet of thermoplastic above its glass transition temperature to orient the molecules. Common film materials are formed by biaxial stretching, where the material is stretched in both longitudinal and transverse directions.

In blow molding, a cylindrical resin called parison is heated, placed in a mold, and inflated by blowing air into the mold from above to create a molded product in the shape of the mold. Figure 1 shows a schematic diagram of blow molding. It is suitable for the mass production of bottled containers, such as PET bottles.

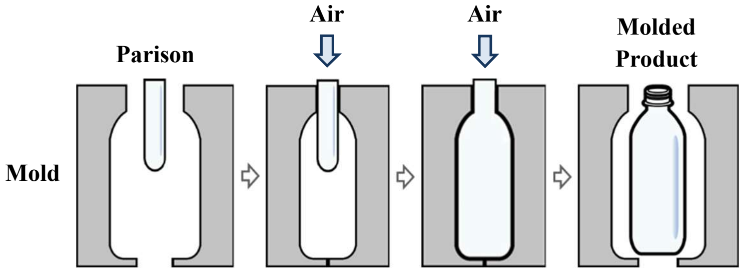

Figure 1 Blow molding

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4. Measurement Results

4-1 Extruded PET sheet and Stretched PET film

Figure 2 shows the measurement results of 1st heating for extruded sheet and stretched film. In the measurement results of extruded sheets, a glass transition with an endothermic peak due to enthalpy relaxation around 75 to 85 °C, an exothermic peak due to cold crystallization around 120 to 160 °C, and an endothermic peak due to melting around 220 to 270 °C are observed. This extruded sheet has a large amount of amorphous because it was formed from molten state into sheet form with a cooling rate close to rapid cooling. Therefore, a baseline shift due to glass transition and an exothermic peak due to cold crystallization were clearly observed. In the measurement results of the stretched film, a small inflection due to glass transition is observed around 80 °C and an endothermic peak due to melting is observed around 200 to 270 °C. However, no exotherm of cold crystallization is observed. This stretched film is a biaxially oriented film in which the molecular chains are oriented by stretching in the longitudinal and transverse directions, and then heat treated to provide dimensional stability. So, crystallization proceeded in the process of stretching and heat treatment, and since there was almost no amorphous, the glass transition was small and the cold crystallization was not observed.

Figure 3 shows the measurement results of 2nd heating for extruded sheet and stretched film. Almost the same DSC curve was obtained for both samples. Both samples were then heated until melting was completely completed at 1st heating, and then quenched to room temperature. This is because the thermal history that the material had during molding process was once erased and the same thermal history of quenching was given to the material. When the material is quenched from the molten state, it becomes solid and mostly amorphous before crystallization occurs. Therefore, the glass transition and the cold crystallization can be clearly observed at 2nd heating.

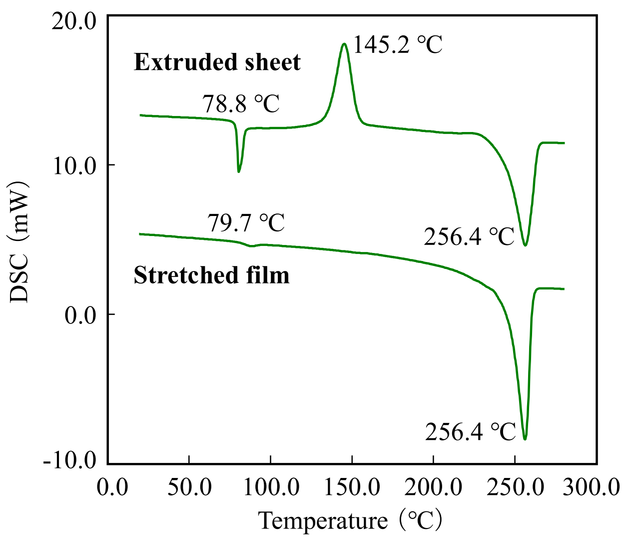

Figure 2 DSC curves of Extruded sheet and Stretched film for 1st heating

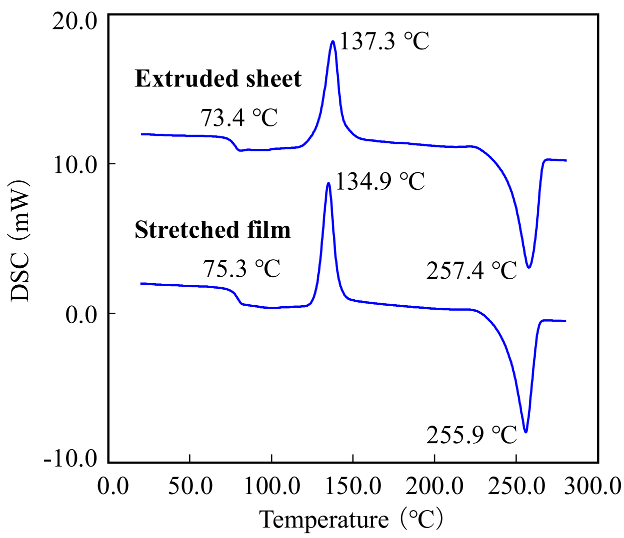

Figure 3 DSC curves of Extruded sheet and Stretched film for 2nd heating

4-2 PET Bottle

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. Even though it is a one-piece molded product, the DSC curve differs depending on the part. In the DSC curves of the screw and bottom, the glass transition, the cold crystallization, and the melting are observed at around 70 to 80 °C, 120 to 140 °C, and 220 to 260 °C, respectively. In both cases, the glass transition and the cold crystallization were observed, indicating that the material is predominantly amorphous. On the other hand, in the DSC curve for the center of the bottle, the glass transition and the cold crystallization are hardly observed, although a melting peak is observed around 220 to 260 °C. In the center of the bottle, the glass transition and the cold crystallization are not observed, indicating that there are mainly crystals. Generally, PET bottles are made by blow molding. In blow molding, the cooling rate during the molding process from the molten state to the bottle form contains a large amount of amorphous because the screw and bottom are cooled at a rate close to rapid cooling. In contrast, the center of the bottle cools at a relatively slow rate, which is thought to have been crystallized during the cooling process, resulting in a highly crystallinity.

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. In this result, the same DSC curve was obtained for every region. As in the case of the extruded sheet and the stretched film described above, the same results were obtained for every region because the heat history that the PET bottle had received during the molding process was erased by heating until the end of melting at the 1st heating and then quenching to room temperature, and the same heat history of quenching was given to the bottle.

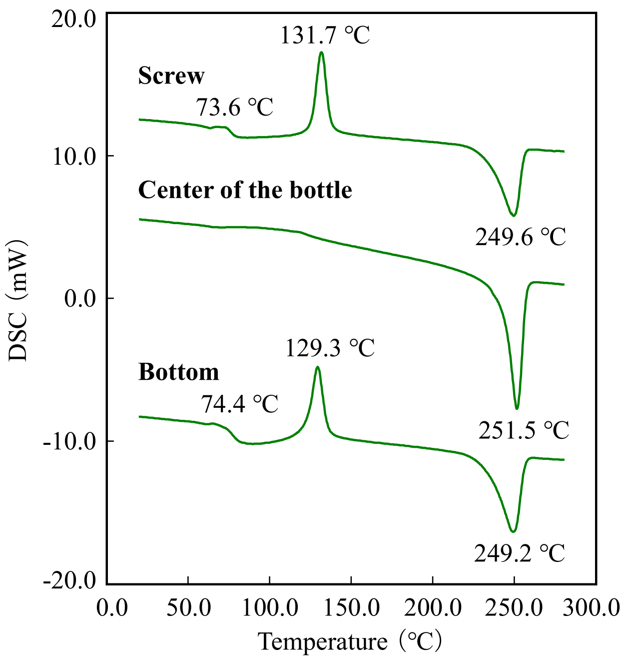

Figure 4 DSC curves of PET bottle for 1st heating

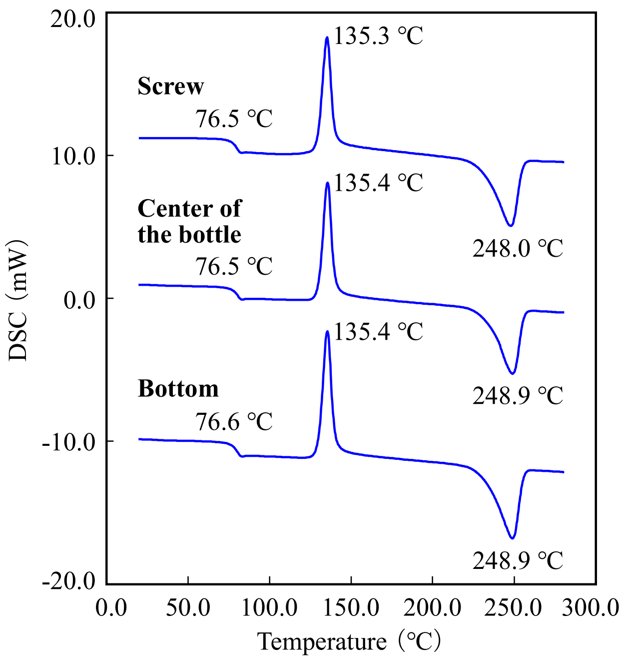

Figure 5 DSC curves of PET bottle for 2nd heating

5. Summary

In this report, as an example of the evaluation of plastic molding products by DSC, measurement examples of three types of PET molded products with different molding methods were introduced.

It can be seen that the same DSC curve can be obtained by applying the same thermal history to samples such as extruded sheets and stretched films, which have different DSC curves due to the difference in molding methods. In addition, as shown in the example of the PET bottle, it was found that even for a one-piece molded product, depending on the molding method and molding conditions, the properties may differ depending on the region.

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