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Application News

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Thermal Analysis

Estimation of Thermal History of Polymer Using DSC-60 Plus Differential Scanning Calorimeter

Introduction

The physical properties of plastics are greatly affected by their thermal history, including the temperature and cooling conditions during molding and the recycling and use environment temperatures of the material. Thermal history refers to the history of temperature changes which a material undergoes. Control of the thermal history of plastic products is extremely important for eliminating product defects and stabilizing product quality. When a defect occurs in a product, a knowledge of the heat environment to which the product was exposed provides useful information for improving defects. It is possible to investigate whether a product was exposed to this type of thermal history or not by using a differential scanning calorimeter (DSC).

In crystalline polymers, there are cases in which an endothermic peak appears near the heat treatment temperature of a sample on the low temperature side from the main endothermic peak caused by melting. However, this type of melting peak is difficult to discover in a DSC curve if it appears as a small inflection point, and not as an endothermic peak. In such cases, it has been reported that a derivative DSC curve is effective. This article introduces an example in which the relationship between the heat treatment temperature and heat treatment time of high density polyethylene was obtained by a technique [(1)] for estimating the heat treatment temperature and heat treatment time from the on-set temperature and peak top temperature of a derivative DSC curve of an endothermic peak which appeared as a result of heat treatment.

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Samples

A commercial high density polyethylene (HDPE) product was used as the sample material. Because the sample material was in pellet form, it was cut into fine particles for use in the measurements.

Measurement of Samples with Various Heat Treatment Temperatures

Seven heat treatment temperatures (80 °C, 85 °C, 90 °C, 95 °C, 100 °C, 105 °C, 110 °C) were used. Approximately 6 mg of the HDPE was placed in an aluminum sample pan, heated from 25 °C to the above-mentioned heat treatment temperature, held for 10 min, cooled to 25 °C at -10 °C/min, and then again heated to 170 °C at 10 °C/min.

Measurement of Samples with Various Heat Treatment Times

Five heat treatment times (10 min, 30 min, 60 min, 90 min, 120 min) were used. Approximately 6 mg of the HDPE was placed in an aluminum sample pan, heated from 25 °C to 80 °C, held for the above-mentioned heat treatment time, cooled to 25 °C at -10 °C/min, and then again heated to 170 °C at 10 °C/min.

Results of Estimation of Heat Treatment Temperature

In measurement of virgin HDPE which was not subjected to heat treatment, a peak is not observed in the derivative DSC curve up to 120 °C (Fig. 1). When heat treatment was conducted at 80 °C for 10 min, an endothermic peak on the low temperature side from the main endothermic peak due to melting was not observed in the DSC curve. However, a peak could be seen in the derivative DSC curve, and the on-set temperature was 80.2 °C (Fig. 2).

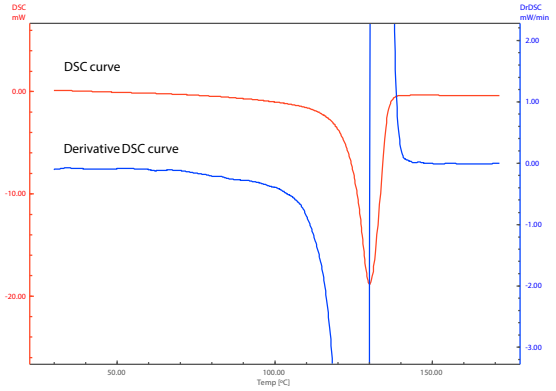

Fig. 1 DSC Curve and Derivative DSC Curve of Virgin HDPE

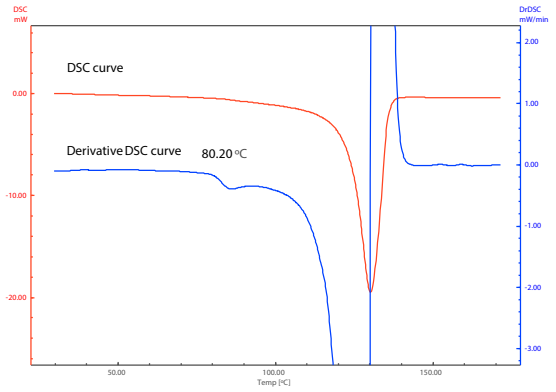

Fig. 2 DSC Curve and Derivative DSC Curve of HDPE Heat-Treated at 80 °C for 10 Min

Next, the derivative DSC curves of the samples heat-treated at temperatures from 80 °C to 110 °C at 5 °C intervals were overwritten, and the on-set temperatures were obtained (Fig. 3). As shown in the relationship between the heat treatment temperature and the on-set temperature in the derivative DSC curves (Fig. 4), extremely good agreement between the two could be confirmed, suggesting that it is possible to estimate the heat treatment temperature from the on-set temperature in the derivative DSC curve.

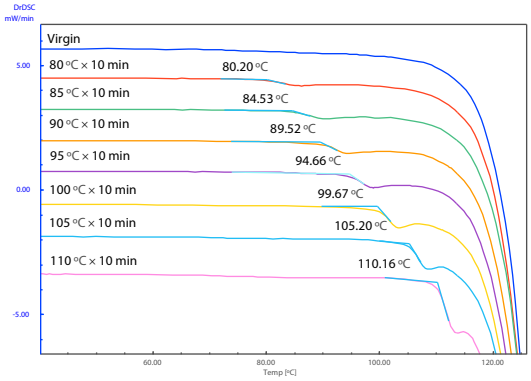

Fig. 3 Derivative DSC Curves of HDPE Heat-Treated at Various Temperatures

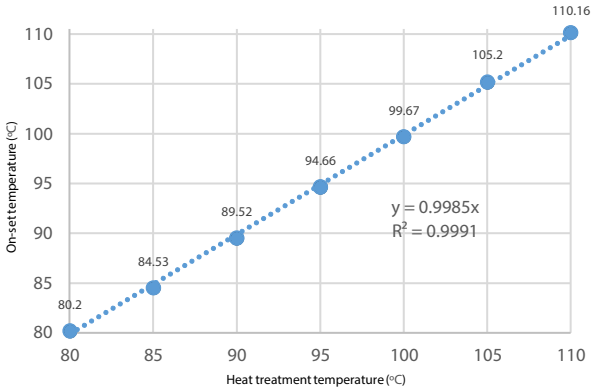

Fig. 4 Relationship between Heat Treatment Temperature and On-Set Temperature in Derivative DSC Curves

Results of Estimation of Heat Treatment Time

The HDPE samples heat-treated at 80 °C for 10 min, 30 min, 60 min, 90 min, or 120 min were measured by DSC, and the peak top temperature of the derivative DSC curves was analyzed.

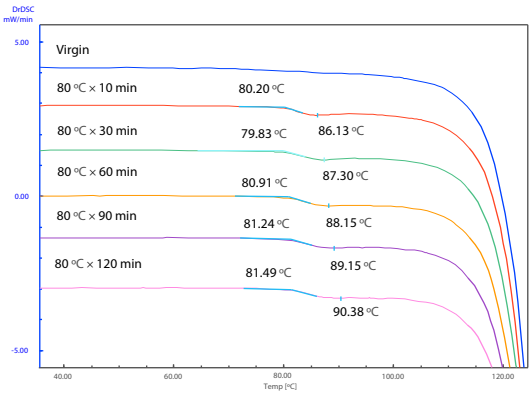

Fig. 5 Derivative DSC Curves of HDPE Heat-Treated at 80 °C for 10 Min, 30 Min, 60 Min, 90 Min, or 120 Min

As the heat treatment time increased, a shift in the peak top temperature of the derivative DSC curves to the high temperature side could be observed (Fig. 5). However, even when the heat treatment time was changed, the on-set temperature showed good agreement with the heat treatment temperature, at 80 °C to 81 °C. Thus, this experiment demonstrated that the on-set temperature is not affected by the heat treatment time. As shown by the relationship between the peak top temperature of the derivative DSC curves and the heat treatment time (Fig. 6), a strong linear correlation between the two was confirmed. This suggests that it is possible to estimate the heat treatment time at 80 °C from the peak top temperature of the derivative DSC curve of HDPE.

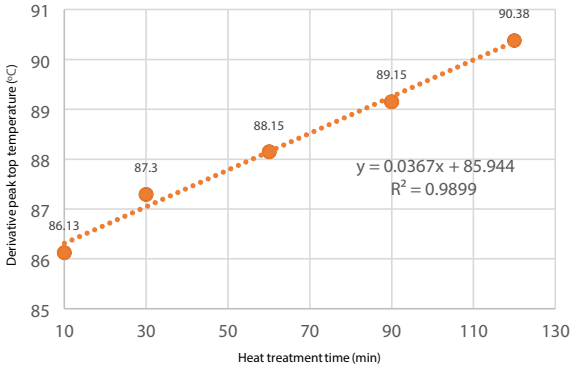

Fig. 6 Relationship between Heat Treatment Time at 80 °C and Peak Top Temperature of Derivative DSC Curves

Conclusion

A method for estimating the thermal histories of materials from the derivative DSC curve was applied to HDPE with satisfactory results. Even when the inflection point in the DSC curve is extremely small and analysis is difficult, a highly sensitive analysis is possible if the analysis is conducted using the derivative curve. The results of these experiments revealed that the on-set temperature displays a correlation with the heat treatment temperature and the peak top temperature shows a correlation with heat treatment time, suggesting the possibility of estimating the thermal history from these values.

<Reference>

(1) Kobunshi Ronbunshu, Vol. 67, No. 9, pp. 511-515 (Sep., 2010)

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