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Application News

No. AD-0091

DSC-60 Plus

Determination of Poly(ethylene terephthalate) Crystallization by Differential Scanning Calorimeter

❑ Introduction

Poly(ethylene terephthalate) (PET) is widely utilized for the production of food and beverage containers as it has low permeability to water and carbon dioxide[1]. As with other semi-crystalline thermoplastic polymers, the physical and mechanical properties of PET depends on the degree and quality of crystallization. The amount of crystallization or percent crystallinity depends on the micro structure and how fast the liquid polymer is cooled during solidification[2]. According to ISO11357-3, DSC can be used to study thermal transitions such as melting, crystallization and glass transition of polymers[3]. This application news examines the crystallinity properties when the liquid PET is cooled at different rates using a differential scanning calorimeter (DSC).

❑ Experimental

A Shimadzu DSC-60 Plus differential scanning calorimeter was used in this analysis. The PET sample was cut into pieces of less than 2 mm size and 5 $\pm$ 2 mg was sealed in an aluminium pan. The aluminium pan filled with alumina was used as reference. The analysis was carried out under inert atmosphere by introducing Nitrogen gas at a flow rate of 50 ml/min into the DSC-60 Plus using a FC-60A Flow Controller.

To erase the thermal history of PET, the sample was first heated to 300^{o}C at a heating rate of 10^{o}C/min. Then, the sample was cooled down to 30^{o}C with a hold temperature of 30 minutes using different cooling rates controlled by the fan in the DSC-60 Plus. Finally, the sample was heated for the second time to 300^{o}C at 10^{o}C/min. The PET was analyzed at least two times for each cooling rate.

❑ Results and Discussion

Figure 1 shows the DSC thermal curves from the second heating of PET subjected to different cooling rates. After cooling to 30^{o}C, and depending on the cooling rate, the PET is in both crystalline and non-crystalline amorphous form. Upon heating to above glass transition at about 76-78^{o}C, the amorphous fraction of the PET becomes more rubbery. Further heating allows PET to crystallize (also known as cold crystallization) at about 145^{o}C which then melts at about 253^{o}C. The area of the positive exothermic peak at 145^{o}C and negative endothermic peak at 253^{o}C represent the heat of cold crystallization and heat of melting respectively. Therefore, the heat of melting also reflects both the crystalline component in the original PET and the portion that crystallized as a result of heating in the DSC.

There are various ways to determine percentage crystallinity of a polymer. The percentage crystallinity is determined from the following equation[4]:

% Crystallinity = (ΔHm /ΔHm^0) x 100% where

ΔHm^0: heat of melting for 100% crystalline PET which is 144.664 J/g [5]

The average data from two analysis for each cooling rate from 300 to 150^{o}C is summarized in Table 1.

Table 1: Comparison between different cooling rates and percentage crystallinity

Cooling Rate	Hc (J/g)	Hm (J/g)	Percentage Crystallinity	Percentage Crystallinity before Cold Crystallization
10^{o}C/min	1.23	36.18	25.0%	24.2%
20^{o}C/min	5.35	35.96	24.9%	21.2%
28^{o}C/min	11.50	34.11	23.6%	15.6%

Generally, faster cooling of melted/liquid PET results in mostly glassy structure whereas slower cooling promotes crystallinity because more time is given to the molecules to arrange themselves into crystals. This could be seen from Table 1 where the percentage crystallinity for 10^{o}C/min cooling rate is

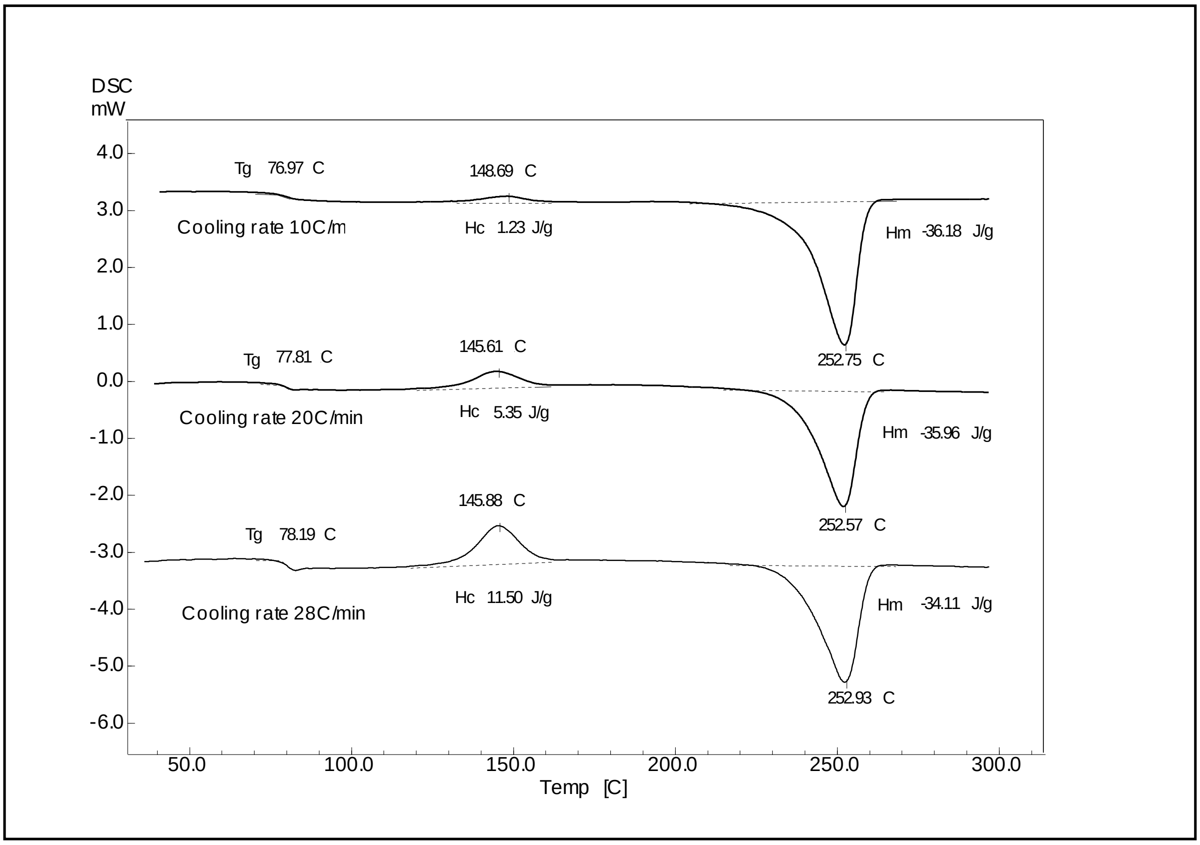

Figure 1: DSC thermal curves from the second heating of PET

25.0% which is higher than 23.6% crystallinity for the faster cooling rate of 28°C/min. There is no difference in percentage crystallinity between 10°C/min and 20°C/min cooling rates.

The "percentage crystallinity before cold crystallization" shows the amount of PET that was already in crystalline state before inducing more amorphous part to crystallize during cold crystallization. The Hm therefore reflects the melting of both the crystalline component in the original PET and the portion that cold-crystallized as a result of heating in the DSC. Hence, to determine the "percentage crystallinity before cold crystallization", the heat of cold crystallization is subtracted from Hm as shown in equation below:

% Crystallinity before Tc =$[(\Delta Hm-\Delta Hc) / \Delta Hm^0]$ 100%
where

ΔHc: heat of cold crystallization (J/g)

Tc: temperature of cold crystallization

The "percentage crystallinity before Tc" is 24.2%, 21.2% and 15.6% for 10°C/min, 20°C/min and 28°C/min cooling rate respectively (Table 1). These results show more crystalline structure is formed with lower cooling rate.

❑ Conclusions

The amount of crystalline content formed when melted PET is cooled down is affected by the cooling rate used. This can be studied using a DSC. Both the percentage crystallinity and "percentage crystallinity before cold crystallization" are higher when lower cooling rate is used.

❑ References

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