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Cooling Studies on Polymer Crystallisation

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Differential scanning calorimetry (DSC) is a common technique that is used to study the thermal transition of polymers when they are heated.[1] Examples of thermal transitions are melting, crystallisation, glass transition and etc.

Polyethylene terephthalate (PET) is widely utilized for the production of food and beverage containers. PET polymer is able to provide good impact resistance, good optical clarity and barrier resistance provided that the polymer achieves a proper amount of crystallinity during production. The amount of crystallisation or percent crystallinity, depends on the molecular structure and on how fast the liquid polymer is cooled during solidification.[2]

In this report, we examined the crystallinity properties of PET pellet sample when it is heated and cooled at two different rates (i.e. slow cooling at -10°C/min and rapid cooling with the use of liquid nitrogen). A Shimadzu DSC-60 controlled by TA-60WS software was used in this analysis. The PET samples were cut into finer pieces and sealed in the aluminium pans. All measurements were carried out under inert nitrogen atmosphere with a flow rate of 10ml/min. The following temperature programming was used:

i. Heating from ambient to 300°C at a rate of 10°C/min
ii. Slow cooling from 300°C to 30°C at -10°C/min or rapid cooling with liquid nitrogen
iii. Reheating from 30°C to 300°C at a rate of 10°C/min

For rapid cooling (a simulated quenching), liquid nitrogen was directly introduced into the cooling unit of the DSC-60 at 300°C and it took about 5 minutes to cool from 300°C to 30°C. For slow cooling, a rate of -10°C/min was set and the rate became non-linear at approximately 100°C and below.

For data analysis, a slight shift in baseline due to a change in heat capacity is taken as glass transition temperature (Tg). There are various ways of determining % crystallinity for a polymer. The % crystallinity, in this report is determined from the following equations:

$$\%\,Total\ crystallinity = (\Delta Hm / \Delta Hm^{\circ}) \times 100\%$$

$$\%\,Crystallinity\ before\ Tc = (\Delta Hm - \Delta Hc)/\Delta Hm^{\circ} \times 100\%$$

where ΔHm: *measured heat of melting (J/g)*
ΔHm°: *heat of melting for 100% crystalline PET*[3] $= 140.1\ J/g$
ΔHc: *heat of crystallisation (J/g)*
Tc: *temperature of crystallisation*

Figure 1 shows the DSC thermogram of the PET pellet subjected to slow cooling. Figure 2 shows the DSC thermogram of the PET pellet subjected to rapid cooling. Table 1 displays the DSC data of the sample measurement during reheating. The total crystallinity for the polymer subjected to slow cooling was determined to be 24.6% whilst the total crystallinity for the rapid cooling case was 22.1%. Generally, rapid cooling results in mostly glassy structure whereas slower cooling promotes crystallinity because more time is given to the molecules to arrange themselves into crystals.[2] In some cases, we are interested to find out the amount of polymer that was already in crystalline state before inducing more amorphous part to crystallize, upon heating to Tc and above. Such crystallinity is determined as the "crystallinity before Tc". The % crystallisation before Tc for slow and rapid cooling was found to be 12.6% and 0.4% respectively. From these results, it is believed that a higher content of the crystalline structure was formed after the slow cooling than rapid cooling.

REFERENCE:

[1]. http://www.psrc.usm.edu/macrog/dsc.htm
[2]. Topics in Material Science (Asymetrix Multimedia Toolbox)
[3]. http://web.utk.edu/~athas/databank/phenylen/pet/pet.html

Samples subjected to:	Tg (°C)	Tc (°C)	Tm (°C)	Heat of crystallisation (J/g)	Heat of melting (J/g)	% Crystallinity before Tc	% Total crystallinity
Slow cooling	77.3	143.7	231.6	16.8	34.5	12.6	24.6
Rapid cooling	77.3	147.0	232.1	30.4	31.0	0.4	22.1

Tg: Glass transition temperature, Tc: Temperature of crystallisation, Tm: Temperature of melting

Table 1: DSC data (during reheating)

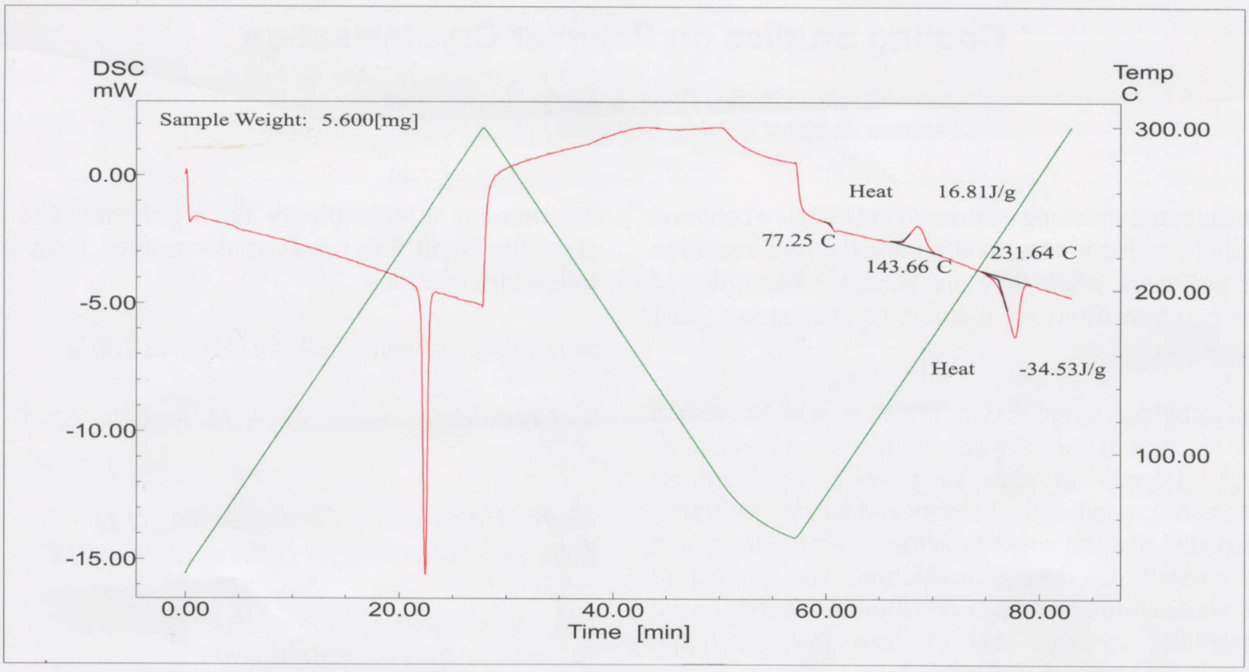

Figure 1: DSC Thermogram (slow cooling)

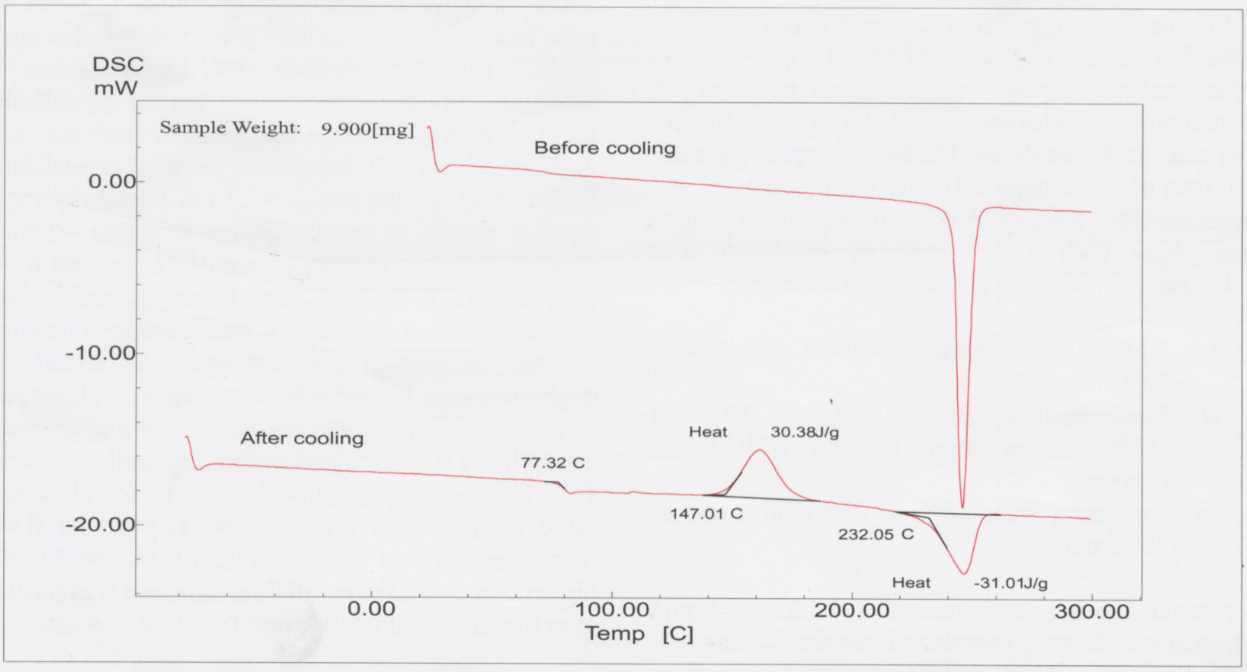

Figure 2: DSC Thermogram (rapid cooling)

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