# DSC as Problem Solving Tool: Measurement of Percent Crystallinity of Thermoplastics

W.J. Sichina, International Marketing Manager

## Introduction

One of the most important properties of semi-crystalline thermoplastics (including PET, nylon, polyethylene, polypropylene, fluoro polymers, PES, PEEK) is the polymer's percent crystallinity. This refers to the overall level of crystalline component in relationship to its amorphous component. The percent crystallinity is directly related to many of the key properties exhibited by a semi-crystalline polymer including:

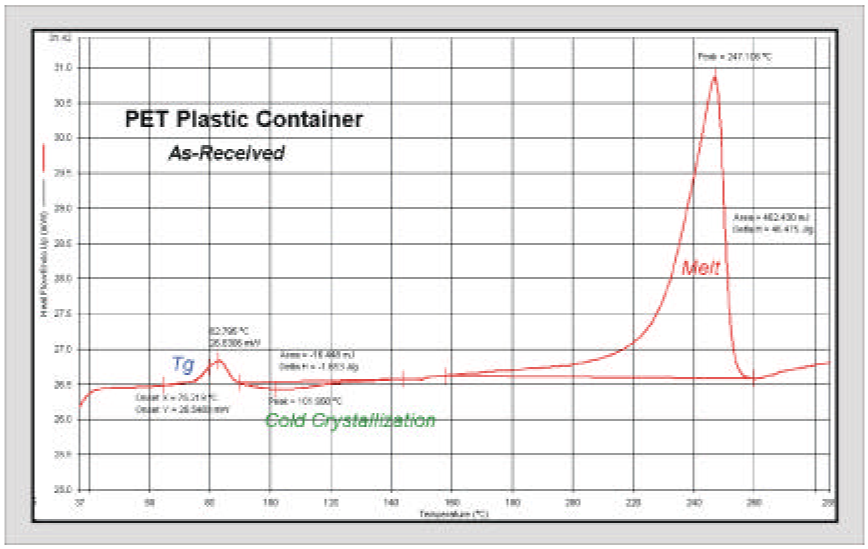
- Brittleness
- Toughness
- Stiffness or modulus
- Optical clarity
- Creep or cold flow
- Barrier resistance (ability to prevent gas transfer in or out)
- Long term stability

Applications where knowing the value of the percent crystallinity are critical include:

- Injection molded parts and components
- Plastic food and beverage containers
- Fibers
- Films
- Automotive components

The assessment of a polymer's percent crystallinity can be most easily performed using differential

*Figure 1. DSC results on 'as-received' PET plastic food container.*




scanning calorimetry (DSC) which measures the heat flow into or from a sample as it is either heated, cooled or under isothermally.

The Pyris 6 DSC from PerkinElmer provides an ideal means of measuring the percent crystallinity of thermoplastic materials. The instrument offers the following important features:

- High performance in terms of sensitivity and resolution
- Low cost
- Outstanding, reliable autosampler for automated loading of up to 45 samples for unattended operation
- Highly stable performance for consistent and reproducible results
- Pyris software (Windows NT-based) for ease of use
- Pyris Player for single button, start-to-finsh operation

PerkinElmer also has available special software, *Temperature Dependent Crystallinity* software, which provides an enhanced and more convenient means of measuring percent crystallinities of thermoplastics.

PerkinElmer™ instruments.

## Measurement of Percent Crystallinity

As an example of the practical importance of knowing the percent crystallinity of polymers, a major food company recently had problems with their plastic ketchup bottles. Some consumers noted that the ketchup bottles contained significantly less ketchup than specified on the label. The state authorities were notified and they verified that the ketchup was not up to specified levels. The ketchup bottles from this particular food company were removed from the store shelves and the company was fined. It was later found that the plastic bottles were defective (due to a greater concentration of recyclates in the plastic) and were less crystalline that they should have been. The lower crystallinity of the bottle permitted the water in the ketchup to seep through to the outside (poor barrier resistance) and this led to the decrease in the weight of the ketchup inside the bottle. Testing of the plastic bottles with DSC would have shown that the bottles were defective with lower than desired percent crystallinity.

To perform this important percent crystallinity measurement, approximately 10 mg of the sample is cut from the test specimen and accurately weighed. The following test conditions are used to measure the sample's crystallinity:

| | |
|---|---|
| Initial temperature: | Room temperature |
| Final temperature: | 30 C above melting temperature of polymer |
| Heating rate: | 10 C/min |
| Purge gas: | Approximately 10 mg |
| Sample pan: | Crimped aluminum pan |

The heats of melting, ΔHm, and cold crystallization, ΔHc, are determined by integrating the areas (J/g) under the peaks. Depending upon the sample's given thermal history, a cold crystallization exothermic peak may or may not be observed during the DSC experiment.

The percent crystallinity is then determined using the following equation:

$$\% \text{ Crystallinity} = [\Delta Hm - \Delta Hc] / \Delta Hm^\circ \bullet 100\%$$

In this equation, the heats of melting and cold crystallization are in terms of J/g. The term ΔHm° is a reference value and represents the heat of melting if the polymer were 100% crystalline. This reference heat of melting has been established for each of the commonly used polymers and some of these are listed below

| Polymer | ΔHm° (J/g) |
|---|---|
| Nylon 6 | 230.1 |
| Nylon 6,6 | 255.8 |
| PET | 140.1 |
| Polypropylene | 207.1 |
| Polyethylene | 293.6 |

The PerkinElmer Temperature Dependent Crystallinity software directly provides these values to make the assessment of the percent crystallinity more convenient and easier.

## Percent Crystallinity Results from PET Container

Polyethylene terephthalate (PET) is widely utilized for the production of food and beverage containers. PET bottle resins provide good impact resistance, good optical clarity and barrier resistance, provided that the resin achieves a proper percent crystallinity during production. PET containers are manufactured using a blow molding process where the resin is melted, injected into a mold were the resin assumes the temporary shape of a tube. Pressurized air is then introduced into the tube, which then expands the shape of the container to its final form. As this occurs, the resin acquires a certain level of crystallinity which then affects the final properties of the container including optical clarity, gas permeability, impact resistance, stiffness, resistance to creep, etc.

Displayed in Figure 1 are the DSC results, generated on the PerkinElmer Pyris 6 DSC instrument, for an 'as-received' PET container.

The as-received bottle resin shows three distinct transitions, all of which are key to the properties exhibited by the container:

Tg or glass transition at 75 C where the resin undergoes softening

Cold crystallization at 101 C (ΔHc = 1.65 J/g) where the polymer undergoes some small amount of crystallization while heating in the DSC

Melting at 247 C (ΔHm = 46.5 J/g) where the existing crystalline component is destroyed

The percent crystallinity of this particular PET food container can be assessed based on these DSC results and based on the theoretical heat of melting for 100% crystalline PET:

PerkinElmer™ instruments.

Visit our website at **www.perkinelmer.com**.

**PerkinElmer Instruments**
761 Main Avenue
Norwalk, CT 06859-0010 USA
Tel: 80O-762-4000 or
(1+) 203-762-4000
Fax: (1+) 203-762-4228

ISO 9001 CERTIFIED

© 2000 PerkinElmer, Inc. Printed in U.S.A.

*Figure 2. DSC results from PET container resin after being annealed at 180 C for 3 minutes.*

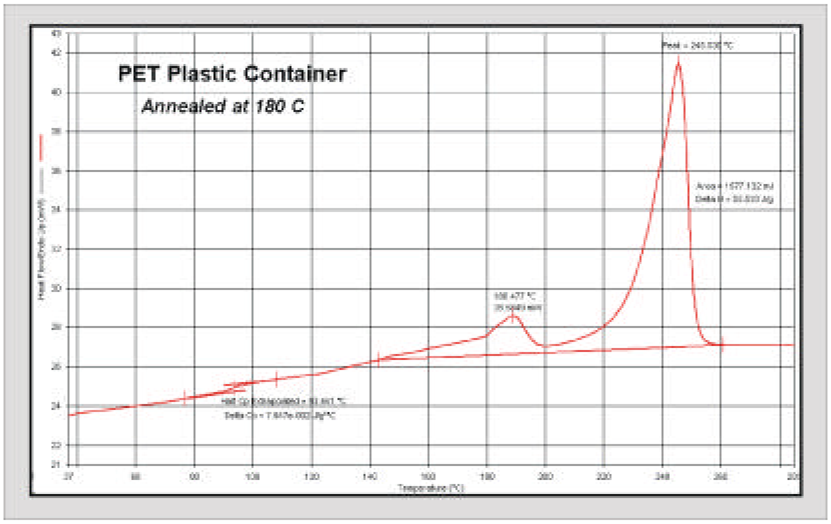
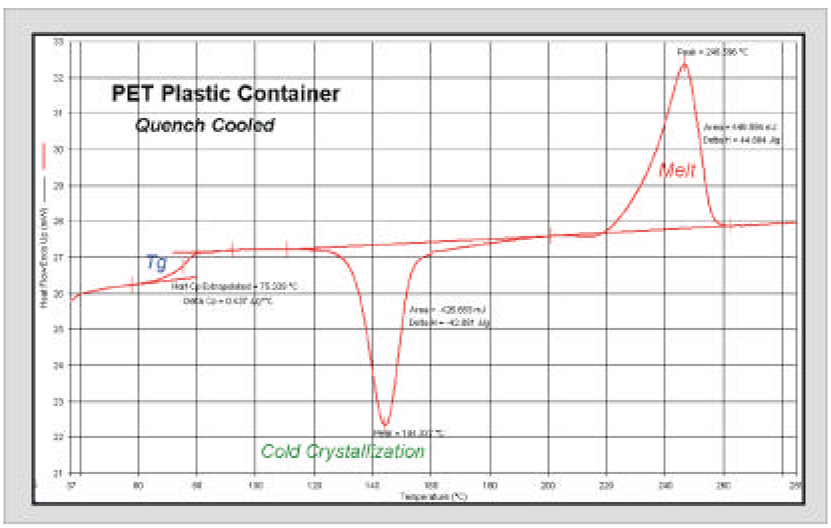



*Figure 3. DSC results on quench cooled PET container resin.*




% crystallinity = (46.5 – 1.65) / 140.1 • 100%

% crystallinity = 32.0%

Knowing this value is critical for a food container as, if the value is too low, the barrier resistance will be low and its creep propensity will be high. Similarly, if the percent crystallinity is too high, the container may suffer with regards to its impact and optical clarity properties.

In order to enhance the properties of the PET resin for certain packaging applications, the blow molded bottle may be held at an elevated temperature between Tg and Tm to stabilize the properties of the resin and to produce an increase in the container's Tg. This will allow the container to be used for more critical barrier resistance uses, such as storage of orange juice, milk and beer. The PET container resin was annealed for 3 minutes at 180 C in order to produce changes in the structure or morphology of the resin and the DSC results for the annealed resin are displayed in Figure 2.

The Tg or softening temperature increased by about 20 C to 93 C, which is important for better storage of gas sensitive liquids such as orange juice or beer

The cold crystallization peak disappears entirely

A heat set, pre-melting endothermic peak is observed at 188 C which reflects the annealing processing step

The overall level of crystallinity of the PET container resin is significantly increased

The percent crystallinity of the annealed container resin is calculated as:

% crystallinity = 55.5 / 140.1 • 100%
% crystallinity = 39.6%

These results demonstrate that the brief annealing step produces a much higher Tg (75 versus 93 C) and a higher crystallinity (32.0% versus 39.6%) for the PET food container.

PerkinElmer™ instruments.

Visit our website at **www.perkinelmer.com**.

**PerkinElmer Instruments**
761 Main Avenue
Norwalk, CT 06859-0010 USA
Tel: 80O-762-4000 or
(1+) 203-762-4000
Fax: (1+) 203-762-4228

ISO 9001

©2000 PerkinElmer, Inc. Printed in U.S.A.

The great sensitivity to PET resin to its given processing conditions may also be demonstrated by quench cooling the resin from the melt, as shown by the DSC results in Figure 3.

The quench cooled PET resin has an extremely low crystalline content and is nearly entirely amorphous. By cooling rapidly from the melt, the PET resin does not have time to develop a significant crystalline component. The DSC measured heat of melting is 44.9 J/g and the heat of cold crystallinity is 42.9 J/g. From this data, the percent crystallinity of the quench cooled PET container is given as:

% crystallinity = [44.9 – 42.9] / 140.1 • 100%
% crystallinity = 1.4% or essentially amorphous (0% crystallinity)

## Summary

The measurement of the percent crystallinity by DSC is a straightforward and easy-to-perform test, which provides extremely valuable information on the end use properties of semi-crystalline polymers. The DSC percent crystallinity is directly related to essential properties including: optical clarity, toughness, stiffness, creep, barrier resistance, gas permeability, and long term stability.

The PerkinElmer Pyris 6 DSC is ideally suited for the measurement of the percent crystallinity as the instrument provides high performance (both sensitivity and resolution), outstanding autosampler, low cost and ease of use with the Pyris software and Pyris Player. The calculation of the percent crystallinity of polymers is made more convenient with the *Temperature Dependent Crystallinity DSC* software offered by PerkinElmer.

PerkinElmer™ instruments.

Visit our website at **www.perkinelmer.com**.

**PerkinElmer Instruments**
761 Main Avenue
Norwalk, CT 06859-0010 USA
Tel: 80O-762-4000 or
(1+) 203-762-4000
Fax: (1+) 203-762-4228

©2000 PerkinElmer, Inc. Printed in U.S.A.

ISO 9001