Better Means of Determining Polymer Crystallinities by DSC: Temperature Dependent Crystallinity Software

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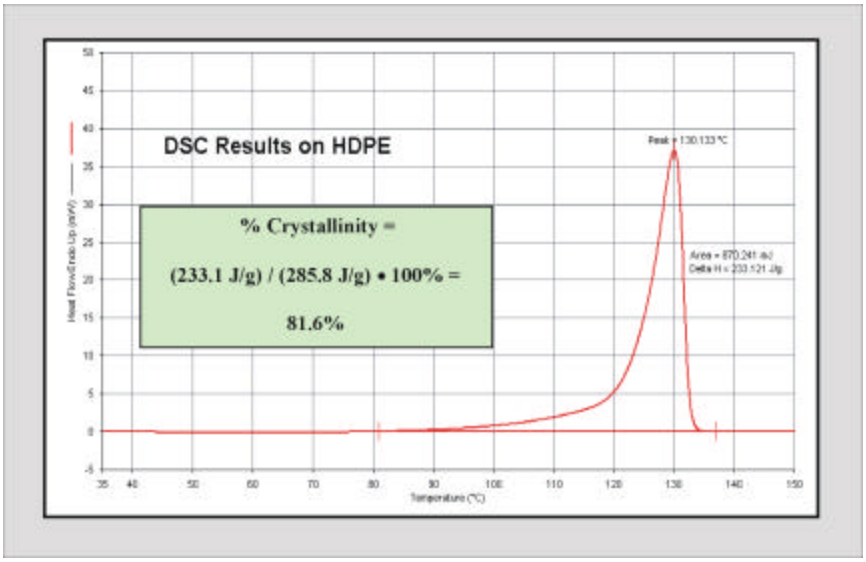
One of most widely used classes of polymers are semi-crystalline thermoplastics. These include polyethylene, polypropylene, polyethylene terephthalate (PET), polybutylene terephthalate (PBT), nylons, and polyether(ether) ketone (PEEK). Semi-crystalline thermoplastics are employed for a wide range of end-uses including garbage bags, transparency films, clothing and carpeting fibers, automotive and aerospace components, videotapes, packaging films and plastic bottles.

Semi-crystalline polymers contain two primary components: a crystalline phase and an amorphous phase. The overall crystalline content of a semi-crystalline polymer depends on several factors including average molecular weight, molecular weight distribution, degree of branching and/or crosslinking, presence of copolymers, concentration of additives, and the thermal history of the polymer formulation. The end-use properties (e.g., impact resistance, barrier resistance, optical clarity, stiffness, dyeability) of products comprised of semi-crystalline thermoplastics are very much dependent upon the overall level of crystallinity achieved by the material during processing. Since the characteristics of products made from semi-crystalline polymers are so dependent upon the level of crystallinity, it is important to have an easy means of measuring this quantity.

Figure 1. DSC results on high density polyethylene showing melting and determination of %.



One of the best analytical means for assessing polymer crystallinities is differential scanning calorimetry (DSC) which measures the heat flow to or from a sample as it is either heated, cooled or held under isothermal conditions. PerkinElmer offers several high performance DSC instruments for a wide range of applications and needs.

Percent Crystallinity

The measurement of a thermoplastic's crystalline content (given as % crystallinity) by DSC is a straightforward and easy-to-perform test. This simply involves taking a small quantity of the polymer (generally 10 mg) and heating it at a rate of 20 C/min through the melting region. The experimental heat of melting (ΔHm) is measured by integrating the area under the melting peak and is then compared to a reference value (ΔHm°), which represents the heat of melting of the theoretical 100% crystalline polymer.

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Shown in Figure 1 is the measurement of the % crystallinity of high density polyethylene (HDPE). The sample melts at 130.1 C and the heat of melting of the HDPE sample is found to be 233.1 J/g. The reference heat of melting, ΔHm°, is 285.8 J/g [1] which yields a % crystallinity of 81.6%,

This simple, but extremely valuable, analysis has been the basis of crystallinity determination used routinely in the characterization of synthetic fibers, packaging films, bottle resins, and injection molded and extruded products. The % crystallinity value is useful for troubleshooting purposes when a thermoplastic does not meet its expected performance. With the growing importance of the incorporation of recyclates into polymer feedstocks, the value of the % crystallinity of the polymer can provide useful information on the effects of the recyclate in the feedstock.

Temperature Dependent Crystallinity

For polymers that undergo cold crystallization when heated, or for those with a broad melting range, a more complex assessment of the crystallinity is required. One valuable approach is the *temperature-dependent crystallinity* method attributed to A.P. Gray [2]. He demonstrated that the weight fraction crystallinity could be obtained from the integrated heat capacity (Cp) data provided that the data for the purely amorphous phase and for the purely crystalline phase are known. At the time of this work, the thermodynamic data to make this method feasible were available for only a few polymers.

The approach described by Gray has been made practical by V.B.F. Mathot [3]. He has developed a method and special software for using DSC heat flow data, together with thermodynamic data from a polymer data bank, to permit determination of the temperature-dependent crystallinity of the most common semi-crystalline polymers, including polyethylene, polypropylene, PET, PBT and nylons.

Theory of the Temperature-Dependent Crystallinity Approach

The temperature-dependent crystallinity assumes that there are two components in a semi-crystalline polymer, the crystalline fraction, *Xc*, and the amorphous fraction, (1 – *Xc*). Mathot has shown that the temperature-dependent crystallinity, *Xt*, can be calculated at any temperature, T, from two experimentally obtained integrals, A1 and A2, from the DSC heat flow data, using the following expression:

$$Xt = [\ A1 - A2\ ] / [Hc - Ha],$$

where Hc is the temperature-dependent enthalpy function of the crystalline phase from the literature, Ha is the temperature-dependent enthalpy of the amorphous phase and A1 and A2 are integrals. The first integral, A1, represents the area between the sample heat flow and the baseline, evaluated from a temperature T up to some point above the melt. The second integral, A2, reflects the area between the extrapolated liquid or melted sample heat flow response and the baseline, evaluated from temperature T to the same temperature above the melt. With the baseline subtracted out, the integration is from the zero (0) milliwatt line.

This complex approach to obtain more informative crystallinity characterization information has been made easy-to-use with the Temperature-Dependent Crystallinity software package offered by PerkinElmer (N520-0050). The software operates with the Windows NT™ or Windows 95™ operating system and the crystallinity software can be used to analyze any DSC data (from any DSC instrument) in ASCII format.

Crystallinity Measurements on PET

One commonly used semi-crystalline thermoplastic material is PET, which is utilized to manufacture synthetic fibers, films and bottles. The physical and mechanical properties of PET are strongly affected by the cooling conditions (thermal history) used to generate the material. PET exhibits a relatively slow crystallization time, as compared to many other polymers, which lets a desired level of crystallinity to be 'dialed in' depending upon the given processing conditions. If PET is cooled quickly enough from the melt, it will be essentially entirely amorphous (0% crystalline). If cooled slowly and allowed to anneal, the crystallinity can approach levels of 40 to 50%. The balance between amorphous and crystalline fractions can be adjusted, via processing, to give the desired thermal and

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Figure 2. Temperature-dependent crystallinity results on a sample of as-received PET fibers.

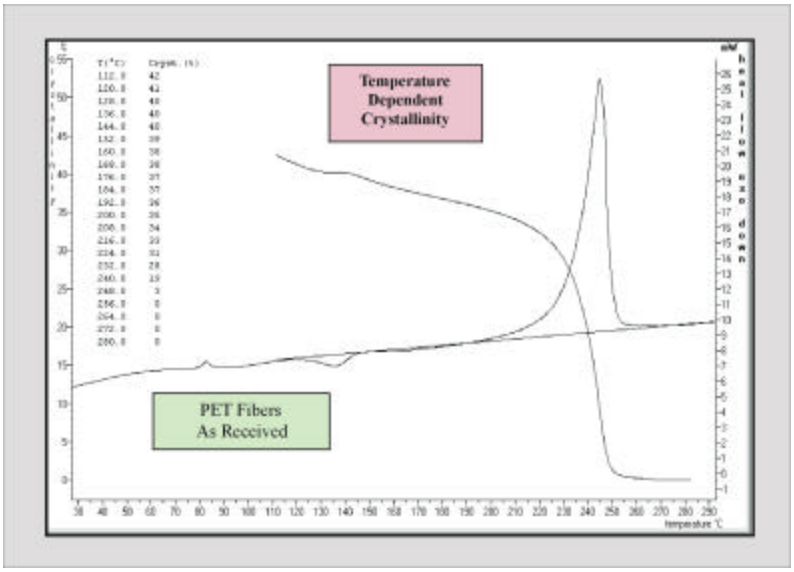
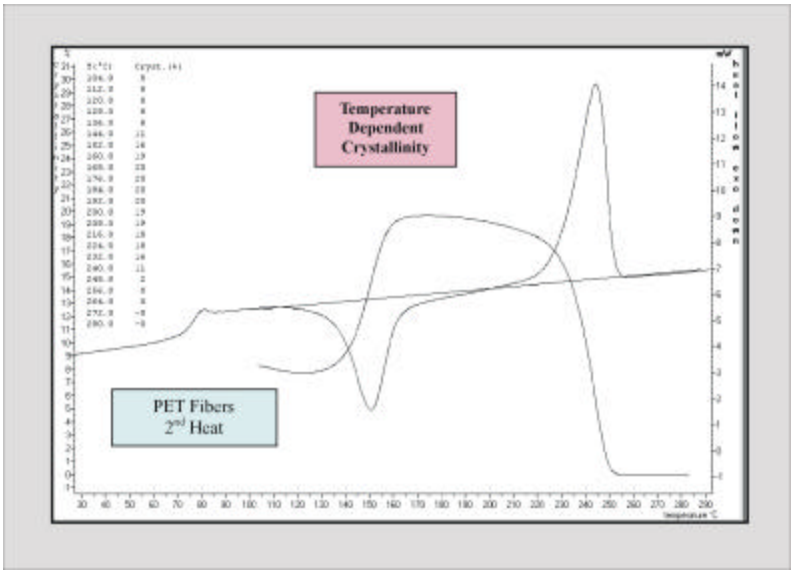


Figure 3. Temperature-dependent crystallinity results obtained on PET fiber sample after melting and cooling (2nd heat).



mechanical properties for the particular end product or application.

With the temperature-dependent crystallinity approach, more accurate results can be obtained on polymers, such as PET, for several reasons:

- If PET is cooled quickly, the polymer can undergo crystallization (cold crystallization) during heating. The heat of melting therefore reflects both the crystalline component in the as-received material and the portion that crystallized as a result of heating in the DSC.
- There is no rigorous way to determine the peak baseline, and the heat of melting is known to be temperature dependent
- Simply subtracting the area of the cold crystallization peak (obtained during heating by DSC) from the area of the melting peak would not give an accurate determination [4].

Shown in Figure 2 are the results obtained using the temperature-dependent crystallinity software for a sample of as-received PET textured yarn. The plot shows the heat flow and the assessment of the temperature-dependent crystallinity as a function of sample temperature.

The PET yarn sample exhibits a glass transition (with enthalpic relaxation peak) at 82 C. The fibers undergo a small amount of cold crystallization at approximately 140 C, as reflected by the occurrence of the exothermic peak. With further heating, the sample undergoes melting and the heat of melting includes the original crystalline fraction plus the additional fraction that occurred while

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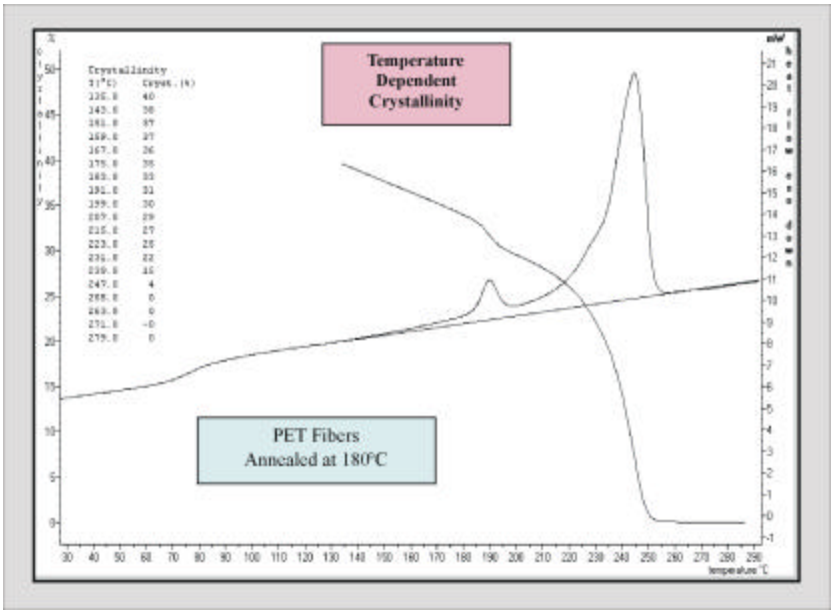
Figure 4. Temperature-dependent crystallinity results on PET fibers after being held at 180 C for 5 minutes.



heating. The table of temperature-dependent crystallinity (displayed on left side of figure) shows that the original crystalline content was a relatively high 42%, which is typical of oriented and heat-set PET yarns. The high crystalline content ensures that the fibers have stable properties.

The PET fibers were then cooled back down directly in the PerkinElmer DSC once they had melted. The low mass furnace permits rapid cooling and allows for the generation of an appreciable amorphous component. The DSC results along with the temperature-dependent crystallinity analysis are displayed in Figure 3 for the 2nd heat (after melting and cooling).

The glass transition event of the cooled PET sample at 78 C is now much more intense (as compared to the as-received fibers) due to the development of a large amorphous component. A large cold crystallization exotherm is observed at 150 C and reflects the large amorphous component in the cooled PET polymer. The temperature-dependent crystallinity analysis reveals that the cooled PET sample had an initial crystallinity of 8%, indicative of a nearly (but not completely) amorphous material.

PET will exhibit a small endothermic peak if the polymer is held or annealed under isothermal conditions at some temperature below the melting transition. It is believed that some of the amorphous phase undergoes crystallization and small, imperfect crystallites develop. The melting of these imperfect crystallites will yield a small endothermic peak below the main melting transition. This is a useful phenomenon, as it allows the processing conditions or thermal history of PET materials to be assessed. For example, in the texturing of PET yarns, the fibers are exposed to an elevated temperature, via a hot plate, to stabilize the properties of the yarn. The texturing temperature and dwell time will produce a small endothermic peak in the yarns that can be detected by a high performance DSC instrument, such as the PerkinElmer DSC. The magnitude and temperature of this heat-set endothermic peak provides valuable characterization information on the processing of the fibers.

Displayed in Figure 4 are the temperature-dependent crystallinity results generated on a sample of the PET fibers which were held at 180 C for a 5 minute period in order to induce the annealing effects.

The annealed PET yarn sample exhibits a glass transition temperature at 80 C. The magnitude (i.e., change in heat flow or heat capacity) of the Tg is small, indicating that the annealed fibers have an appreciably large crystalline content. This is borne out by the temperature-dependent crystallinity results, which shows that the annealed fibers have an initial crystallinity of 40%. The annealed PET sample yields a small pre-melting endothermic peak at 188 C, which is reflective of the heat set conditions that the yarn received in the DSC prior to running the sample. The temperature-dependent crystallinity curve reflects this transition as a decrease in the level of crystallinity over this temperature range.

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Summary

DSC has been used for many years to successfully determine the crystallinity of semi-crystalline polymers. The standard test simply involves measuring the heat of melting and comparing this heat to a known reference value. This method has been enhanced and extended to determine the initial crystallinity of polymers with broad melts or those undergoing crystallization below the melt. This temperature-dependent crystallinity method uses a straightforward and thermodynamically rigorous approach that has been placed into special PerkinElmer DSC Crystallinity software (N520-0050). This software can be used with files obtained from any DSC instrument. The method can be performed rapidly, without special equipment or special operator training. The approach is useful for both R&D and QA purposes.

References

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