Application Note P0-001

Percent Crystallinity – XRD
PE (low density) film

Percent crystallinity of polymers is commonly determined via XRD (x-ray diffraction), although DSC (differential scanning calorimetry) is also commonly used. XRD uses the total x-ray scattering of both the crystalline and amorphous phases to determine the crystallinity, and no external standard is needed. DSC uses the heat of crystallization compared to the total heat given off by a certain weight of a polymer material to determine the crystallinity (e.g. a standard is necessary). XRD provides a more accurate result, and assuming all data collection and processing variables are controlled, XRD provides very precise relative comparisons between samples.

When XRD is used to determine crystallinity of polymeric materials, the greatest possible source of error is frequently related to the preferred orientation of the polymer. Typical line or point source XRD instruments fail to observe large sections of the Debye ring, and therefore essential peak intensity is missed and the relative intensities of the crystalline peaks are misrepresented. Therefore, it is essential to use a 2-dimensional detector, capturing the intensity variation around the Debye ring, as shown in figure 1 below. This 2D detector image shows the significant preferred orientation of the orthorhombic polyethylene, and the hkl s of the reflections are shown on the figure.

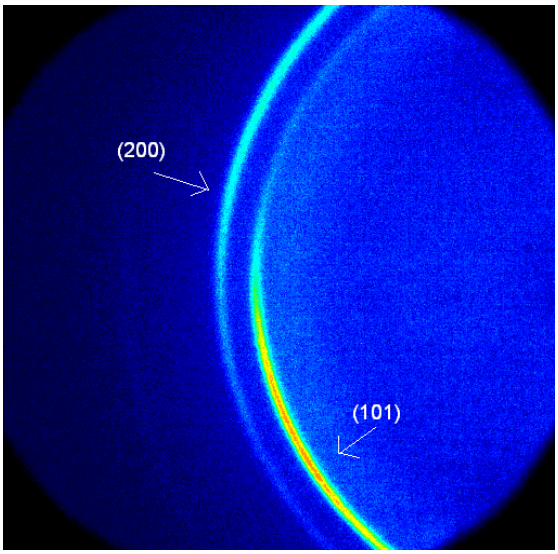


Figure 1: 2D detector image of (101) and (200) hkls showing preferred orientation.

Cell constants:
a: 7.4, b: 4.93, c: 2.534
α,β γ = 90°
density of amorphous material: ~0.825 g/cc,
density of crystalline material: ~ 0.980 g/cc

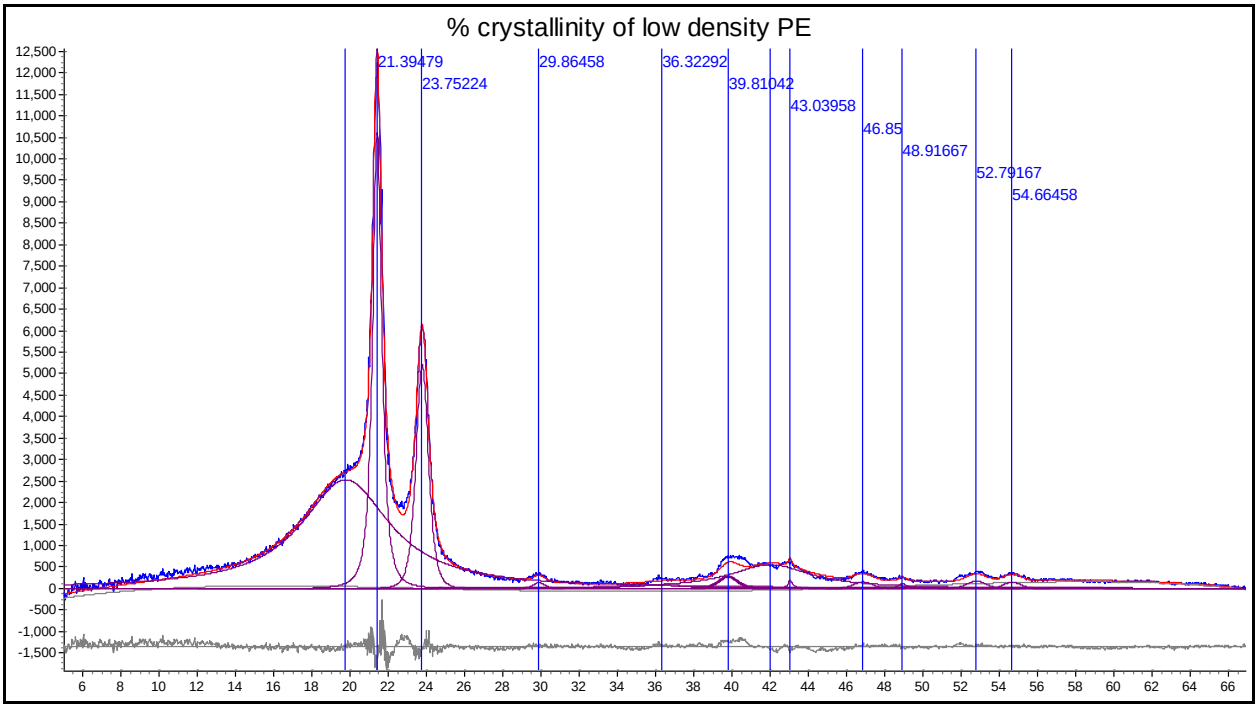
When percent crystallinity is determined via XRD, the crystallinity is calculated by dividing the total area of crystalline peaks by the total area under the diffraction curve (crystalline plus amorphous peaks).

% Crystallinity = (total area of crystalline peaks) / (total area of all peaks)

Air scatter must be removed prior to profile fitting of peaks, and air scatter is typically determined by running a “blank” (e.g. collecting a data pattern under identical conditions without a sample in place) and subtracting that blank pattern from the pattern of the sample under investigation. Compton’s scatter, which is inelastic (non-diffraction) scattering, is typically approximated and removed since it is not related to the crystalline or amorphous scatter. If air scatter and Compton’s scatter are not taken into account, the reported percent crystallinity will be biased to lower calculated crystallinity.

It should also be noted that the exact locations of the amorphous and crystalline regions are typically left to the judgment of the diffractionist. The refinement model should account for all intensity in the pattern, and should account for all amorphous and crystalline regions. Figure 2 shows the refinement and % crystallinity calculation for the low density PE as calculated by the Topaz Rietveld Refinement software from Bruker. Crystalline peak locations are labeled for clarity.

Figure 2: Peak locations and profile fitting for percent crystallinity



After peaks are assigned as crystalline or amorphous, the percent crystallinity is easily calculated as shown in the equation above. In this case, three amorphous regions are defined, at approximately 19°, 42° and 58° in 2θ. The first amorphous peak, typically located between 18° and 20° in 2θ, is occasionally referred to as “para”-crystalline in the literature. Depending upon the FWHM (full width at half maximum) of this peak, this scattering entity be displaying chain ordering in one or two crystallographic directions, but has not developed well formed three dimensional crystallites. Therefore it may be

considered to be intermediate between amorphous and crystalline. If the diffractionist chooses to define the peak as para-crystalline, the calculation for percent crystallinity can be done by either excluding this peak from the calculation (e.g. it is not assined to crystalline or amorphous intensity and is simply excluded), or it can be assigned as crystalline intensity. For the purposes of this example, this leading peak of PE was assigned as amorphous. The total percent crystallinity is calculated to be 53% as shown in figure 3 below.

Figure 3: Topaz output for percent crystallinity calculations