Powder X-ray Diffraction Basic Course Eighth Installment: Crystallinity

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Abstract

In the eighth lecture of the Powder X-ray Diffraction Basic Course, we will describe "Crystallinity." Crystallinity is a parameter that indicates the degree of crystallinity of a sample, such as a pharmaceutical or polymeric material, and can be estimated from a powder X-ray diffraction (PXRD) pattern. It is defined as the ratio of the crystalline phase to the total weight (crystalline phase+amorphous phase). The percent crystallinity (reported as %crystallinity) is evaluated from the difference in profiles between crystalline and amorphous phases. In this paper, we describe a method for calculating the crystallinity by decomposing peaks using a profile fitting method. This method is performed by separating diffraction peaks from the crystalline phase and haloes due to scattering from the amorphous phase, and using the integrated intensity obtained by profile fitting. This method does not require pure crystalline and amorphous materials. However, the results can be influenced by the analyst's subjectivity, as the crystallinity varies depending on how the halo is estimated. High reproducibility values can be obtained independent of the analyst by carefully selecting the parameters that determine the background estimation and the peak shape of halo.

1. Introduction

Crystallinity is a parameter that indicates how many crystals are contained in a material. In other words, it indicates the degree of structural order in a sample. Determining crystallinity is required in a wide range of industrial fields. For example, crystallinity is one of the most important parameters in drug development because it directly affects solubility and stability(1). In addition, it is known that the proportion of crystalline phases in polymer materials is related to their mechanical strength and physical properties(2). Crystallinity can be evaluated using the profile fitting method in X-ray diffraction. This will be possible if the diffraction pattern of the crystalline phase can be separated from the interference scattering intensity curve (halo) of the amorphous phase (Fig. 1). The measurement can be performed by either the reflection or transmission method, but there are some points to be considered. For example, the analysis allows some flexibility in setting conditions, such as the analysis range and background determination. As a result, the analyst's discretion may influence the results(3). In addition, as crystallinity increases, the halo's intensity decreases, making it harder to distinguish. This increases the difficulty of the analysis.

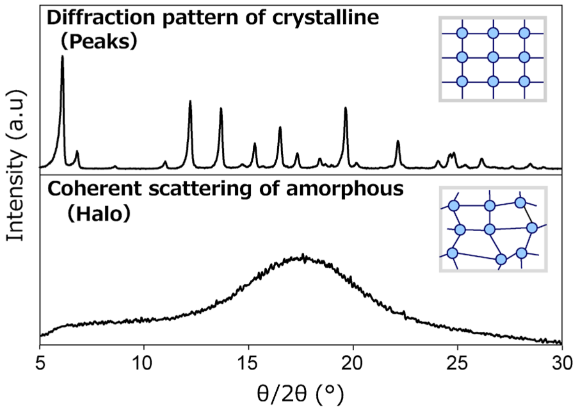

Fig. 1. Example of crystalline phase and amorphous profiles.

In this paper, the method for calculating crystallinity, points to be considered, and measurement and analysis advice will be presented with actual examples.

2. How to Calculate Crystallinity

The total scattering intensity of X-rays is the sum of the background intensity due to air scattering, incoherent scattering, and coherent scattering. The intensity of the incoherent scattering is always constant regardless of the state of the material (gas, liquid, amorphous, or crystalline). Therefore, crystallinity can be calculated by separating the crystalline phase's diffraction from the amorphous phase's scattering in the X-ray diffraction pattern.

Crystallinity (x_c) is calculated using the following equation, based on the sum of the scattering intensity from the crystalline phase (I_c) and the amorphous phase (I_a).

$$x_c = \frac{I_c}{I_c + I_a} \qquad (1)$$

In this case, the following conditions are assumed to be satisfied.

1. Chemical components of the crystalline and amorphous phases are identical.
2. The halo, which is the scattering curve from the amorphous phase, can be clearly observed.
3. In principle, materials with different compositions are not mixed.

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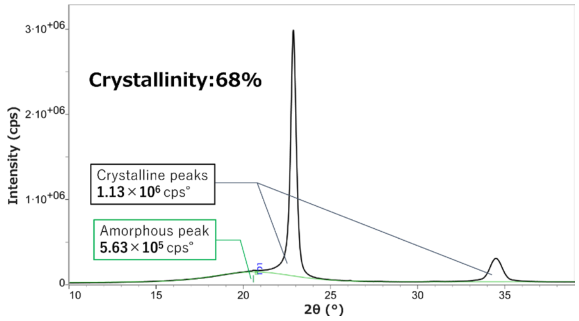


Fig. 2. Crystallinity by peak separation of POM.

If these conditions are not met, the calculated values may significantly differ from the true values(3). A measurement method to reduce the effect of orientation is explained in Section 4.

Figure 2 shows an analysis example of polyacetal (POM) resin, which is a type of engineering plastic. Sharp diffraction peaks, which come from the crystalline phase, are observed around $2\theta=23°$ and $34.5°$. On the other hand, a broad halo is observed around $2\theta=20.5°$. Crystallinity was calculated based on the integrated intensities of the diffraction peaks and haloes. As a result, the measured crystallinity of POM was 68%.

3. Measurement

3.1. Sample Preparation

Reflection measurement using the BB method is commonly used for powder samples. In this section, setting the slit width and the X-ray penetration depth in the reflection measurement are discussed.

When X-rays are irradiated over an area wider than the sample width, diffraction peaks from the sample holder are detected. In particular, a halo from the glass sample holder is observed around $2\theta=20$–$30°$, as shown in Fig. 3. Therefore, when using glass sample holders, it is necessary to set the incident and length-limiting slits appropriately so that the X-ray irradiation does not exceed the sample area. Details of each slit setting are described in "Powder X-ray Diffraction Basic Course|Third Installment: Sample preparation and measurement conditions to obtain high-quality data(4)". Please refer to it for further information.

For samples composed of only light elements with low X-ray absorptivity, such as organic materials, haloes and diffraction peaks due to the sample holder are observed, as shown in Fig. 3. This is because the incident X-rays reach the bottom of the sample holder. If an Al sample holder is used, measurement for crystallinity is possible in the 2θ range below the Al 111 diffraction peak. However, in the case of glass sample holders, the halo from the holder is mixed with the halo from the sample. Therefore, it is recommended to use zero-background holders in which diffraction peaks are not detected(5).

3.2. Oriented Sample

Crystallinity can be calculated using the profile fitting method without pure crystalline or amorphous reference materials. This approach is also applicable in cases where diffraction peaks and the amorphous halo overlap. However, it is difficult to obtain reproducible intensities from oriented samples, such as organic materials, leading to variations in the calculated crystallinity.

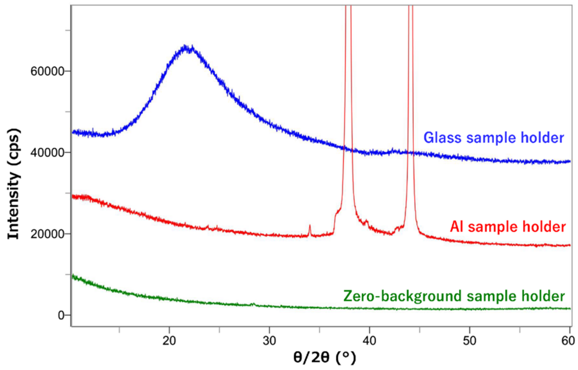


Fig. 3. Diffraction pattern from glass sample holders, Al sample holders and zero-background sample holders.

Polymers are typical examples of materials that are easily oriented. Nonetheless, if the crystal orientation is the same, it is possible to evaluate crystallinity as a relative comparison between samples. In polymeric materials processed into fibers or films, diffraction peaks corresponding to specific crystal plane orientations are strongly observed. These peaks originate from molecular chains aligned along the elongation direction(6). This section describes the measurement method for stretched polymer fiber samples in detail.

For such samples, transmission measurements are performed using an *αβ* attachment or a fiber sample holder with a spinning mechanism in the transmission optics. Spinning a sample reduces the influence of intensity ratio changes caused by orientation. However, thin polymer samples increase background noise during transmission measurements at low angles. This makes it difficult to acquire sufficient intensity and results in long measurement times. To compensate for this disadvantage, this section introduces a transmission measurement using a two-dimensional wide-angle X-ray scattering (2D-WAXS) system equipped with a HyPix-3000 two-dimensional detector.

The optical system for the 2D-WAXS transmission measurement is shown in Fig. 4. This system covers a range of $2\theta=6.5$–$35°$ and can collect the full circumference of Debye–Scherrer rings by positioning the detector at a short distance of 27 mm from the sample. In contrast to the conventional scan mode, 2D-WAXS optics measures using exposure mode with a fixed two-dimensional detector. As a result, it is possible to simultaneously integrate intensities corresponding to the width of the detector, and each measurement can be completed within a few minutes. In addition, by measuring the full circumference of the Debye–Scherrer rings, it becomes possible to visually grasp both the particle conditions and structural anisotropy of the sample(7).

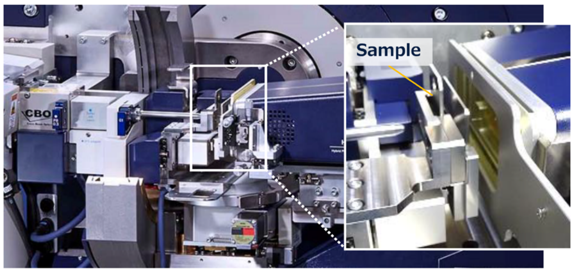


Fig. 4. Transmission 2D-WAXS optical system (camera length 27 mm).

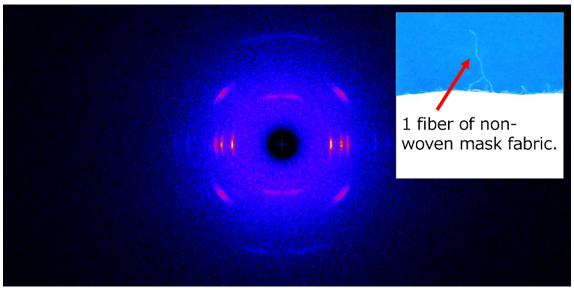


Fig. 5. Example of 2D-WAXS measurement of polypropylene fiber.

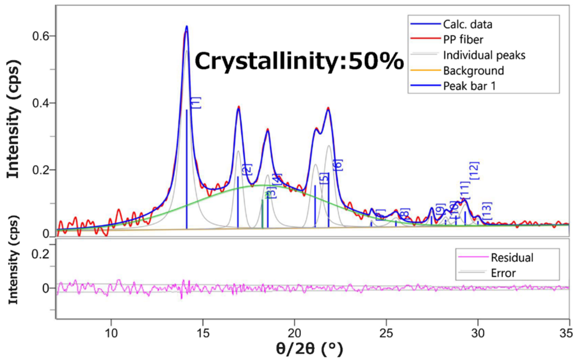


Fig. 6. Crystallinity analysis of polypropylene fiber.

A measurement example is shown in Fig. 5. In this case, a single 20 µm polypropylene fiber that was extracted from a nonwoven mask was measured using the 2D-WAXS optical system. The diffraction image showed only partial Debye–Scherrer rings, indicating a high degree of orientation in the fiber. By subtracting the blank data, only the diffraction intensities originating from the fibers can be extracted. The calculated crystallinity in this case was 50% (Fig. 6). These results demonstrated that the 2D-WAXS transmission method allows quantitative evaluation of crystallinity even in single fibers through exposure measurement.

4. Analysis Procedure

In peak separation using the profile fitting method, the analysis is conducted by decomposing the X-ray pattern into diffraction peaks originating from the crystalline phase and a broad halo from the amorphous phase. Generally, the halo profile overlaps with the diffraction peaks of the crystalline phase. The higher the crystallinity, the more difficult it is to separate the halo from the diffraction peaks of the crystalline phase because of its reduced contribution to the diffraction pattern. In such cases, the position and shape of the halo must be estimated by the analyst, which introduces a degree of subjectivity into the analysis. In this section, we explain the analysis procedure illustrated in Fig. 7, using the SmartLab Studio II software.

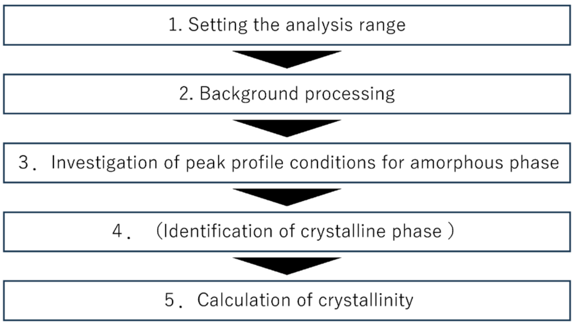


Fig. 7. Crystallinity analysis procedure.

4.1. Setting the Analysis Range

In general, for qualitative analysis using powder X-ray diffraction, measurements are conducted up to approximately $2\theta=60°$ for organic materials and up to $2\theta=90°$ for inorganic materials$^{(5)}$. On the other hand, most crystallinity measurements are performed from the 2θ angle where the first crystalline diffraction peak appears to the 2θ region where an amorphous halo can be clearly observed. This range is sufficient for use in relative comparisons between samples. However, it is essential that the measurement range includes the entire baseline of the amorphous halo to avoid background subtraction errors. This is discussed in the following section.

4.2. Background Processing

Minimizing background intensity is crucial for enhancing the detection sensitivity of trace diffraction peaks. Diffraction patterns often show an increase in background intensity in the region below $2\theta=40°$, which is mainly due to air scattering. Since such scattered radiation affects the accuracy of the analysis value, appropriate countermeasures are essential.

Here are three countermeasure examples:

1. Adjusting the slit width to ensure that the X-ray beam does not exceed beyond the sample width at the start measurement angle.
2. Using a scattered radiation protector or knife-edge to reduce the influence of air scattered rays.
3. Subtracting the background signal of the sample holder from the diffraction pattern.

After implementing these measures, it is important to apply an appropriate background correction during data analysis.

The background is typically defined as a baseline connecting intensities on the low-angle side and high-angle side. Commonly, background correction involves

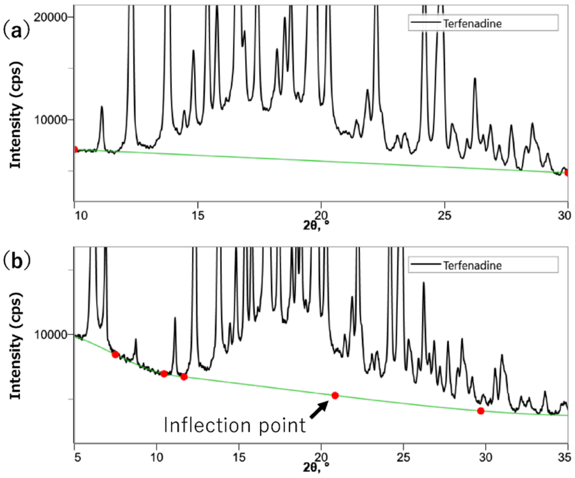


Fig. 8. Background processing with (a) Line connecting endpoints and (b) B-spline.

drawing a straight line between the endpoints of the diffraction pattern. This method is relatively robust against operator bias. Figure 8(a) illustrates this approach, where the background is defined by a straight line connecting two points at both ends, marked by red circles. In this case, analysts are advised to carefully select endpoints located in stable intensity regions-areas where the signal is constant or nearly constant and free of diffraction peaks.

Alternatively, when the background is elevated at low angles side, a more flexible approach, such as background fitting using a B-spline function, is effective, as shown in Fig. 8(b). In this method, too, analytical error can be minimized by reducing the number of inflection points and ensuring the background line forms a smooth and adequate curve in stable background regions.

4.3. Investigation of Peak Profile Conditions for the Amorphous Phase

The diffraction patterns of samples with low crystallinity make it easier to observe a halo clearly, and the analysis errors are relatively small. Therefore, when multiple samples with varying degrees of crystallinity are available, it is recommended to analyze the sample with the lowest crystallinity first. In such cases, the estimated halo peak position (2θ) should be treated as a fixed parameter for the subsequent analyses of the other samples in order to reduce the risk of analytical error.

If the halo is obscured by diffraction peaks originating from crystalline phases and its shape cannot be reliably identified, it is advisable to fix the values of the asymmetry factor and attenuation (or decay) factors during analysis. The asymmetrical factor gives the symmetry of the peak shape and typically approaches 1.0 for halos due to their high degree of symmetry. The attenuation factors, ηL/mL and ηH/mH, describe the tailing of the peaks on the low-angle and high-angle sides, respectively. These two values generally range between 0.5 and 1.0, and show similar values in typical diffraction peaks.

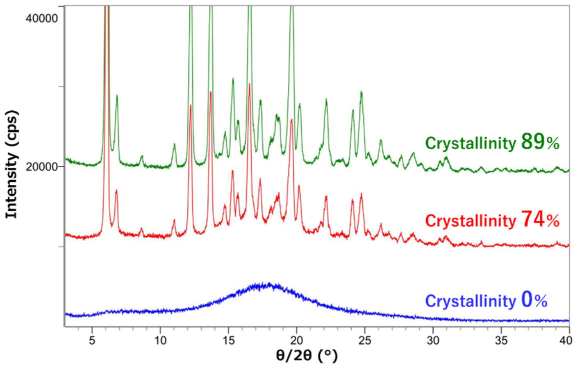
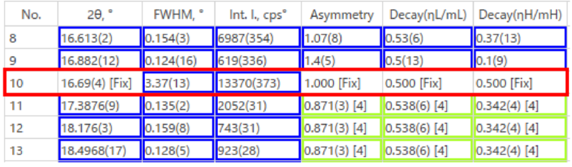


Fig. 9. Example profiles of terfenadine with different crystallinities.



No.	2θ, °	FWHM, °	Int. I., cps°	Asymmetry	Decay(ηL/mL)	Decay(ηH/mH)
8	16.613(2)	0.154(3)	6987(354)	1.07(8)	0.53(6)	0.37(13)
9	16.882(12)	0.124(16)	619(336)	1.4(5)	0.5(13)	0.1(9)
10	16.69(4) [Fix]	3.37(13)	13370(373)	1.000 [Fix]	0.500 [Fix]	0.500 [Fix]
11	17.3876(9)	0.135(2)	2052(31)	0.871(3) [4]	0.538(6) [4]	0.342(4) [4]
12	18.176(3)	0.159(8)	743(31)	0.871(3) [4]	0.538(6) [4]	0.342(4) [4]
13	18.4968(17)	0.128(5)	923(28)	0.871(3) [4]	0.538(6) [4]	0.342(4) [4]

Fig. 10. Example of edited parameters.

An example of halo peak for fitting conditions is shown in Fig. 10. As shown in the accompanying table, parameters such as peak position, full width at half maximum (FWHM), asymmetry factor, and attenuation factors were fixed. By refining only the integrated intensity, inter-analyst variability can be suppressed. This also allows for consistent quantification of the halo even in highly crystalline samples where it is not clearly visible.

4.4. Identification of Crystalline Phase and Calculation of Crystallinity

As mentioned in Section 2, crystallinity analysis does not necessarily require the identification of the chemical composition of the sample, provided that all samples share the same composition. SmartLab Studio II automatically recognizes the remaining diffraction peaks as crystalline phases when a halo is detected as an amorphous phase in the diffraction pattern, and then calculates the crystallinity.

5. Example of Crystallinity Analysis of Low-density and High-density Polyethylene

Polyethylene (PE) is one of the most widely used polymer materials due to its excellent processability and relatively low cost. Depending on the reaction conditions during synthesis, PE can be produced with varying densities, resulting in different types, such as low-density polyethylene (LDPE) and high-density polyethylene (HDPE). The density of PE is closely related to its mechanical properties, and crystallinity is commonly used as an indicator for evaluating these characteristics (8).

Figure 11 shows the diffraction patterns of HDPE and

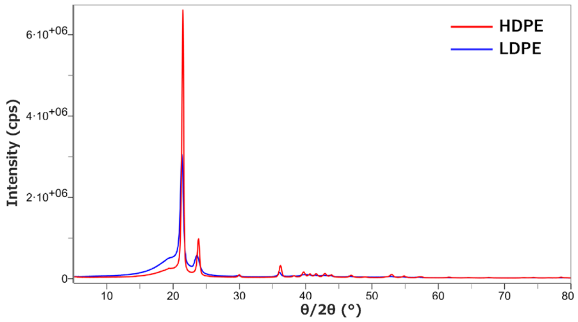


Fig. 11. Profiles of HDPE and LDPE.

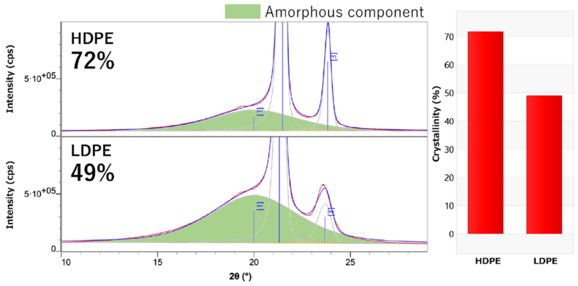


Fig. 12. Crystallinity of HDPE and LDPE.

LDPE, measured using a Bragg-Brentano optics system. Peak top position of a halo attributed to the amorphous phase was observed around $2\theta=19$–$20°$ in both profiles. The 2θ range from 10° to 29°, which includes both the strongest diffraction peak and the amorphous halo of PE and has a relatively flat background, was selected for crystallinity analysis.

Crystallinity was analyzed following the procedure outlined in Section 4. The results showed crystallinity values of 72% for HDPE and 49% for LDPE, as indicated in Fig. 12. Compared to HDPE, LDPE exhibits a slight shift of the diffraction peak to a lower 2θ angle. Therefore, the profile shape of the halo was fixed, but the 2θ position was not constrained. The analysis was conducted using the template function in SmartLab Studio II, which enables consistent evaluations and is expected to improve analytical accuracy.

6. Conclusion

In the eighth lecture of the Powder X-ray Diffraction Basic Course, we explained crystallinity analysis through specific measurement examples. The analysis software SmartLab Studio II includes dedicated crystallinity functions and offers enhanced usability, such as batch processing of multiple datasets using analysis templates.

To ensure highly reproducible crystallinity evaluations, it is essential to acquire high-quality diffraction data. This article has outlined key considerations for conducting accurate crystallinity analysis. For further details on selecting an appropriate optical system and important considerations during measurement, please refer to Powder X-ray Diffraction Basic Course, "Selection of equipment configuration to obtain high-quality data" and the third installment, "Sample preparation and measurement conditions to obtain high-quality data."

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