

STUDENT: Materials are often classified as crystalline, semi-crystalline, or amorphous. Most polymers are semi-crystalline. This means a fraction of the material is amorphous and lacks order in arrangements of polymer chains, while the remainder of the material exhibits parallel, well-ordered chains that define crystalline regions.

There are several methods for determining the degree of crystallinity in a polymer. X-ray diffraction can be used to determine degree of crystallinity, because intensity of X-ray diffraction reflection is proportional to the material density. An X-ray diffraction pattern displays both sharp Bragg's peaks, arising from the crystalline portion, and a broad diffraction peak caused by scattering from the amorphous portion of the polymer. The degree of crystallinity can be determined using this formula, where the total integrated intensities, all of the sharp peaks, are divided by the integrated intensities of all peaks, including that of the amorphous peak.

Many laboratories have access to XRD peak fitting software that can be used to calculate degree of crystallinity. But this software can often be expensive. I set out to create a peak fitting software to calculate degree of crystallinity for semi-crystalline polymers using Mathematica.

The basic idea for this program is that the user will define a series of Gaussian peaks using this equation. The width, the height, and the exposition of these peaks can be manipulated.

This code allows the user to adjust the appearance and position of multiple peaks, and match it to an existing XRD pattern. First, the code allows the user to adjust the position and the scale of the XRD pattern. The user is then able to adjust the positions of both the crystalline peaks and amorphous peaks.

Once the user obtains a fit that they're happy with, they can calculate the degree of crystallinity by determining the integrated area under the crystalline peaks, divided by the integrated area under all of the peaks. In this particular polymer, the determined degree of crystallinity was 41%.

To test the accuracy of my code, I fit XRD patterns for polyethylene varieties with known values for degree of crystallinity. The polymers for which I chose to match XRD patterns were

low density polyethylene, high density polyethylene, and ultra high molecular weight polyethylene. The expected value for degree of crystallinity for low density polyethylene is 44% to 51% crystallinity. The value obtained using Mathematica peak fitting was 46% crystallinity, so this is within the accepted range.

Similarly, the expected value for degree of crystallinity for high density polyethylene is 48% to 69% crystallinity. And Mathematica peak fitting obtained a value of 56% crystallinity.

Finally, ultra high molecular weight polyethylene has an expected value of 75% to 77% crystallinity. Mathematica peak fitting showed a value of 76% crystallinity.

In all three polymer case studies, this code obtained a degree of crystallinity value within the acceptable range, indicating manual Mathematica peak fitting of XRD plots is a reasonable way to determine a material's degree of crystallinity.

The code I just described showed a way to import an XRD pattern as an image and manually fit the peaks to calculate degree of crystallinity. However, I can do a better job of determining degree of crystallinity if I let the user's peak selections be a starting guess, and let Mathematica find the best set of Gaussian curves to fit the data.

One of the challenges with this method is I have to take data that's currently saved as a JPG image and convert it into something Mathematica can use to find a best fit. So the way I do this is I import my JPG image here. And then I use that, and I convert it to be either black or white. Then I'm able to determine the locations of the black pixels and isolate them.

However, my lines really thick, which means that at each x position, I have multiple y positions. So then I'm able to use the following code to choose whether I want to have the mean y position at each x value, or one of the highest y positions at each x value. After my data is in this form, I'm able to use it for future curve-fitting applications.

So after I have data, I'm able to write code that allows the user to input guesses for where they think the peaks should be located. And then Mathematica uses a function called Find Fit, that's going to find the best approximation for my data given the guesses and the model I give it to work with. So this model is a model that includes three different Gaussian peaks.

So the full code is available to you in my notebook. But here's the final product. Like in the previous curve-fitting program I showed you, you're able to adjust the positions and shapes of the crystalline peaks and the amorphous peaks as follows. Once you think you have a fit that's

fairly reasonable, you can click Find Nearest Solution, and Mathematica is going to help you find the best fit for this data. Then, using these Mathematica found values, you can calculate degree of crystallinity for the curve.

So in conclusion, degree of crystallinity can be determined from XRD patterns. And today I demonstrated two possible ways of doing this in Mathematica. There's a fair amount of background code that goes into the outputs you saw today. And all this code is available to you in my Mathematica notebook. Hopefully you'll find it very easy to modify to meet your unique application needs.