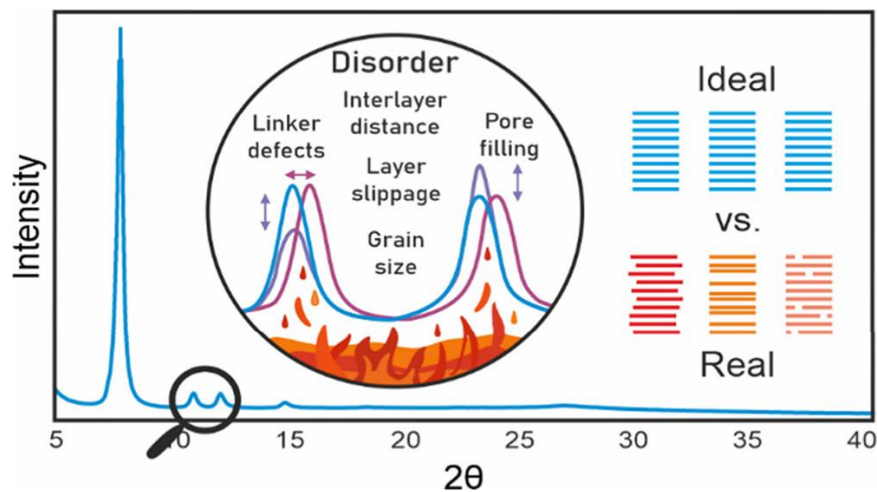


## Outlook and best practice

Whilst PXRD can inform a lot about the structure of a 2D COF, the pattern can be more complex than initially anticipated due to various structural effects. It is imperative to work within the limitations of the refinement model and to use other characterisation techniques in tandem for the most accurate structure resolution.



## Context

- A typical 2D COF PXRD pattern contains ~3–5 peaks. Peak positions, shapes and intensities all contribute to information about the atomic structure (e.g. stacking).
- However, **not all COFs form the idealised structure**.
- Many structural effects influence the pattern: particulate size, pore filling, trapped solvents, layer slippage, linker/node defects, interlayer spacing.
- These lead to peak broadening and/or shifting, and changes may cancel.

## Structural effects

- Particulate size: **Smaller** particulates lead to **broadened, more symmetrical** peaks.
- Layer slippage: **Larger** offset in slippage causes **increased** peak **broadening**. COFs with larger pores require larger offsets to broaden the peaks.
- Linker and node defects: If **randomly distributed** throughout the structure, these will not break the COF symmetry, so **no peak broadening**. Defects will change peak intensities, however.
- Interlayer spacing: Causes peak **broadening** and peak **shifting**.

## Refinement methods

- **Refinement** refers to adjusting a proposed crystal structure, so the calculated diffraction pattern gives the best match to experiment.
- Single peak fit: take **one peak** and refine the unit cell dimensions, scale factors, background, peak shape and intensity values. Atomic positions are **not** refined.
- Pawley refinement: Refines the same parameters as above but **all peaks are refinable**, considered individually. Useful as a first guess.
- Rietveld refinement: **Most detailed**, allowing for refinement of atomic positions as well as the parameters above. Peak intensities are calculated based on the unit cell contents, allowing for intensity ratios to be retained.
- Weighted profile reliability factor (Rwp), expected reliability factor (Rexp) and goodness of fit (GOF) can all be used to assess refinement quality.