

A new “chain” of events: polymers in the Powder Diffraction File™ (PDF®)

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(Received 7 February 2014; accepted 19 February 2014)

Developments in X-ray analysis, and advances in scientific research, have dramatically influenced the types of data now considered suitable for inclusion in the Powder Diffraction File™ (PDF®). Initially, the PDF was geared towards the identification of unknown crystalline materials by comparison of d-spacings and peak intensities. Today, the International Centre for Diffraction Data (ICDD) maintains and continuously enhances the quality and content of the PDF database to better provide customers and scientists with a comprehensive reference source that supports their needs, and interests. The events that initially led to the inclusion of crystalline polymer data to the PDF have recently been amended to also encompass semi-crystalline and amorphous polymeric materials as well. This paper discusses the resultant updates being made to the PDF in support of this new data form, and also highlights several features and benefits of providing this data to PDF users. © 2014 International Centre for Diffraction Data. [doi:10.1017/S088571561400013X]

Key words: polymers, powder diffraction file, X-ray analysis

I. INTRODUCTION

Current entries in the Powder Diffraction File™ (PDF®) represent a significant fraction of the world's crystallographic data. These data are received from several different sources, converted into a standard format and editorially reviewed by experienced scientists using International Centre for Diffraction Data (ICDD)'s four-tiered processes, compliant with ISO 9001:2008 standards (ICDD, 2012). The ICDD also maintains a series of strategic partnerships with crystallographic database organizations, which enables the production of this comprehensive reference database, used for identification of the large range of materials often encountered in the diffraction community. Within this reference containing over 783 000 (inorganic + organic) unique entries, numerous subfiles have been developed to optimize the usefulness of the PDF. Among them is the polymer subfile (POL) that is currently being populated with polymer and polymer-related materials.

In recent years, a wide range of applications have been discovered for polymers based on their ability to form composites possessing tailored properties. Polymers are, therefore, often encountered during analysis of these mixed phase materials, and as a result require a method for identification when using common material characterization techniques. Researchers have found X-ray diffraction (XRD) to be an effective method for characterizing polymers because of its ability to perform non-destructive analysis and to provide crucial information about the degree of ordering in materials. The usefulness of XRD in the study of solid substances lies in its ability to distinguish between ordered and disordered states (Alexander, 1969). For polymers and polymer-composites, this distinction is vital as many of their properties are inherently correlated to and affected by a materials' polymeric

state. For many polymer applications, it can be important to find the right balance of amorphous content to crystalline content in order to optimize a material's physical properties. In addition, the polymer chain length, extent of branching, cross-linking, and tacticity all play distinct roles in the properties of a polymer. Various physical properties are often easily affected by adjustments to the structural order of a polymer; including elasticity, optical transparency, strength, durability, or any combination of the aforementioned. In general, polymers containing microcrystalline domains possess higher impact resistance and tend to be tougher than polymers that are fully amorphous. Therefore, the optimal ratio of amorphous to crystalline material must be uniquely defined to optimize the physical properties of interest.

Historically, the PDF has contained entries constructed as reduced diffraction pattern representations (also known as d-I lists: list of d-spacings and intensities) for phase identification. Having d-I lists reduced storage space requirements, and increased search speed capabilities. However, as technology advanced, storage space and speed capabilities have become less limited, and over time the file has evolved to where it is now common practice to construct entries of full digital patterns, containing 2000–10 000 data points. These changes have greatly improved the capability of using the PDF for phase identification of crystalline materials. However, when the phase of interest is amorphous or semi-crystalline, a d-I list and/or atomic coordinates will not adequately define the amorphous profile observed in a diffraction pattern. To allow for improved whole pattern analysis, particularly when amorphous phases are present, the PDF now includes digital raw data patterns, referred to as PDF experimental patterns (PD3s), for amorphous, semi-crystalline, and crystalline phases. An example of the benefits of a PD3 pattern of cellulose I β compared to a stick pattern produced from a d-I list for the same material is presented in Figure 1. The PD3 shows that the cellulose I β is semi-crystalline (possessing crystalline and amorphous components), and that the crystallite size is small

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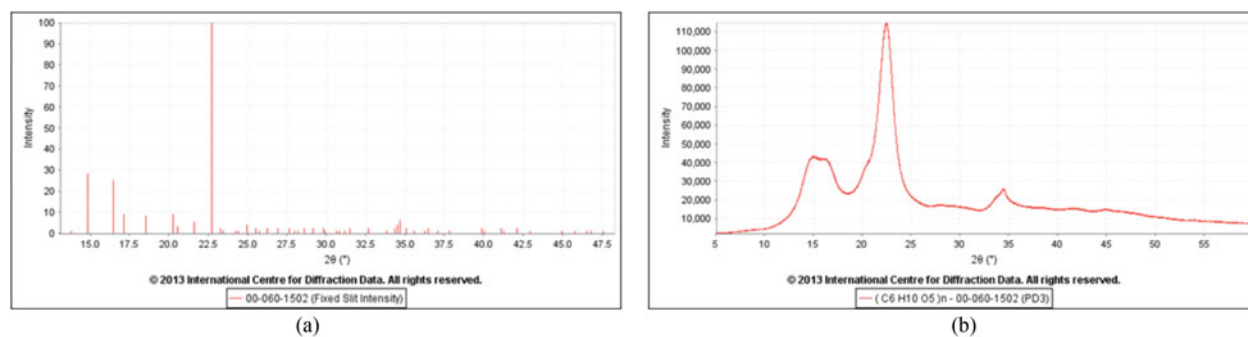


Figure 1. (a) Stick pattern and (b) raw data (PD3) representation for cellulose I β . This example displays how raw data patterns for polymers cannot always be accurately determined from a d-I list alone. (Color online)

(indicated by broad diffraction peaks). PD3 patterns are also beneficial when analyzing clays, glasses, and nanomaterials.

II. DISCUSSION

To date, the polymer diffraction data included in the PDF has consisted of a targeted group of materials. This group includes high-volume commercial polymers, or polymers often encountered during XRD analyses such as various celluloses, polyolefins, polyesters, nylons, etc. The objective is to provide the user with high-quality references for polymers used in commercial applications. The PDF cards for polymers generally include the following:

- Nominal chemical formula and name
- Preparation details
- Data collection conditions
- d-I list(s)
- Reference(s)
- Physical properties
- PD3
- Supplemental data (*when available*)

Determining the best method for including polymers in the PDF provided some challenges as it required some adjustments to our standard processes of data acquisition as well as editorial review. Typically a PDF entry is assigned a quality mark based on several criteria; one of which is the quality of the compound's d-I list. However, for semi- or non-crystalline polymers it can be problematic to accurately extract d-I lists for materials where peaks are relatively broad and limited in number. In addition the d-spacing may no longer correspond to the interatomic layer distance but to a peak maximum from incoherent scattering. This made it impractical to rank some semi- and all non-crystalline polymers using the same methods as utilized for crystalline materials. As a result, new quality marks, "G" and "M", were added to the quality system to designate entries containing significant amorphous content.

Minimally Acceptable (M). *Indicates the material has significant amorphous content, and has a digital diffraction pattern with a good signal-to-noise ratio. However, no chemical analysis data to support the material's composition was provided.*

Good (G). *Indicates the material has significant amorphous content, and has a digital diffraction pattern with a good*

signal-to-noise ratio. Additionally, some chemical analysis information has been provided to support the specified composition of the material (i.e. spectroscopy, pair distribution functions, commercial source, etc).

For all "G" and "M" patterns, a digital raw data pattern is provided because, as seen in Figure 1, it can often provide better insight into the polymeric state, relative percent crystallinity, and orientation/ordering of a material, than that which could be determined with a typical d-I list. Providing polymer reference patterns with various states of crystallinity should enable researchers to do crystallinity analyses and allow for improved characterization of the amorphous/crystalline states.

Population of the "POL" subfile with amorphous and semi-crystalline experimental patterns began with release 2011 and progressively increases each year (Figure 2).

III. DATA USAGE/PROCESSING

Sample data referenced in this article were acquired from various sources; (i) data contributed by the authors, and/or (ii) data selected from a pool of polymer entries in the POL subfile of the PDF (ICDD, 2013).

A. Search/match (S/M)

One of the major benefits of having polymers in the PDF-4 database is the ability to carry out S/M, processes on multiphase unknowns containing polymers. The S/M process in PDF-4 utilizes algorithms to successively identify phases and reanalyze the residual pattern until multiple phases have been identified. The PDF-4 not only provides high-quality reference patterns for phase identification of these individual polymer phases, but with its S/M capabilities, also has the potential to drastically improve total pattern analysis with powder XRD. PDF S/M tools can be used to identify the polymer of interest as well as any filler, stabilizing agent, or other chemical component. Polymer entries have been present in the PDF since 1945 (Set 03) and the d-I listings have historically been useful in the identification of crystalline polymers. The first patterns included materials such as paraffin wax and cellulose. The inadequacy of using d-I list(s) for non-crystalline and semi-crystalline polymers was recognized by Turley during her work at Dow Chemical Company. As a result, she constructed a book containing full XRD patterns for many commercial polymers, homopolymers, and copolymers being used at that time (Turley, 1965). This book provided

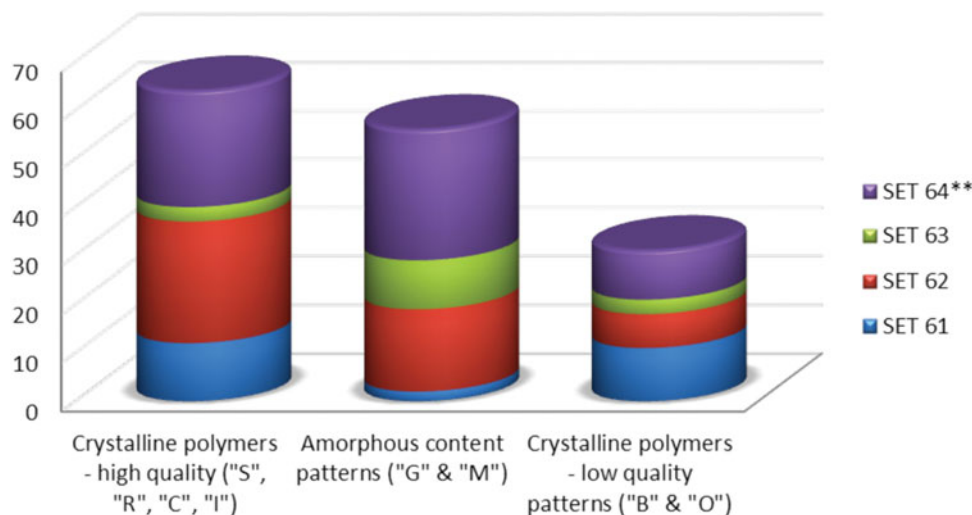


Figure 2. Recent growth of patterns in the “POL” subfile that contain amorphous content; based on the distribution of quality marks. ** Quality mark distribution projection for upcoming release of PDF-4 (purple). (Color online)

useful references for identification of polymers by visual comparison, and became a standard reference for phase identification for scientists working in polymer research. Now, with the progression of the POL subfile to new digital formats, polymer diffractionists now have access to a quality digital, international reference database that can be used as a primary identification tool, which is continually edited, reviewed, and annually updated. The digital format of PDF also enables users to carry out studies of crystallinity, amorphous scatter, orientation, and crystallite size.

Figure 3 illustrates the usefulness of this new subfile at work, showing the S/M results for experimental powder XRD data that were processed using PDF-4. A scientist attempted to analyze an opaque film that was initially thought to contain only semi-crystalline poly(ethylene terephthalate) (PET). However, after performing the data collection the scientist noticed several unexpected peaks were present. To identify

these peaks, data were imported into PDF-4, and overlaid the PD3 for the known phase of biaxially oriented PET film. A S/M was executed on the remaining unknown peaks, which were successfully identified as a common phase of TiO_2 .

The polymer data in PDF-4 generally used for phase identification can also be a method of providing the user with insight into the material’s degree of crystallinity. Through proper analysis of powder XRD patterns of polymers, one can extract valuable percent crystallinity information for a specified material. Additionally, changes to structural ordering within a polymer can be particularly evident just from visual inspection of the powder XRD pattern. When a polymer possesses a low degree of crystallinity, the structure is rarely defined by a crystalline model, which results in diffraction patterns that typically exhibit very broad, indistinct features [Figure 4(a)]. Crystallinity generally improves as a polymer’s structure becomes more ordered; often from

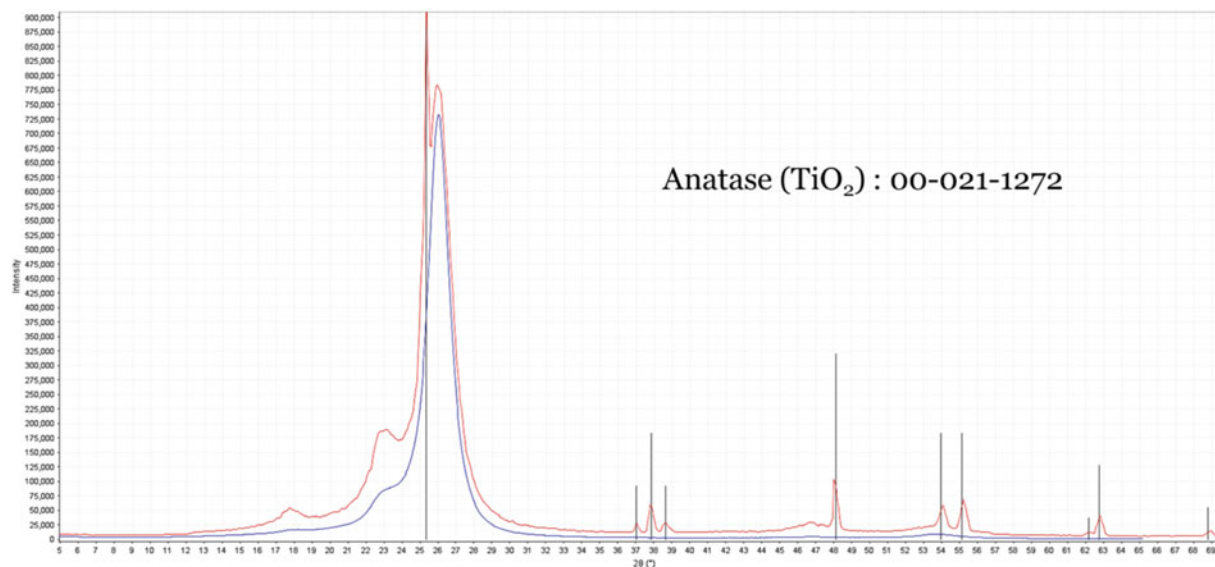


Figure 3. Search/match processing in PDF-4 of a PET film containing an unknown. The unexpected peaks were identified as anatase (TiO_2). The blue pattern represents a PDF experimental pattern of biaxially oriented PET. (Color online)

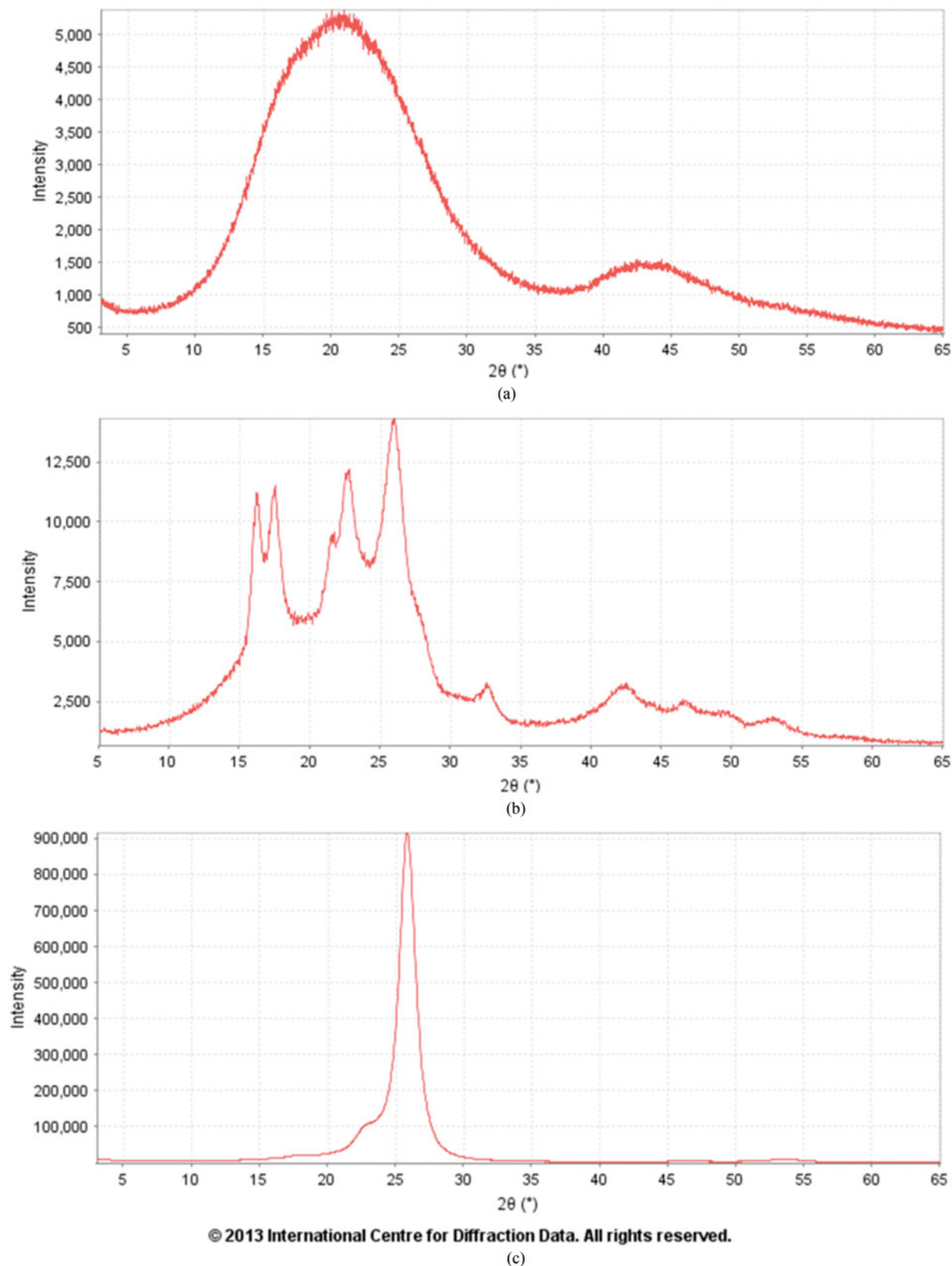


Figure 4. Example of variations that occur in X-ray diffraction patterns as PET film is converted from its amorphous phase (a), to a thermally crystallized phase (b). Additionally, (c) represents a strain induced crystallized phase powder diffraction pattern for oriented PET film that underwent sequential biaxial stretching during processing. (Color online)

variations to its processing. This often results in narrower, well-defined peaks in the XRD pattern [Figures 4(b) and 4(c)]. With the digital raw data patterns for polymers being

stored in the PDF-4 as PD3s, users will now be able to discern valuable information to properly identify these types of structural changes, as well as acquire some foresight into how

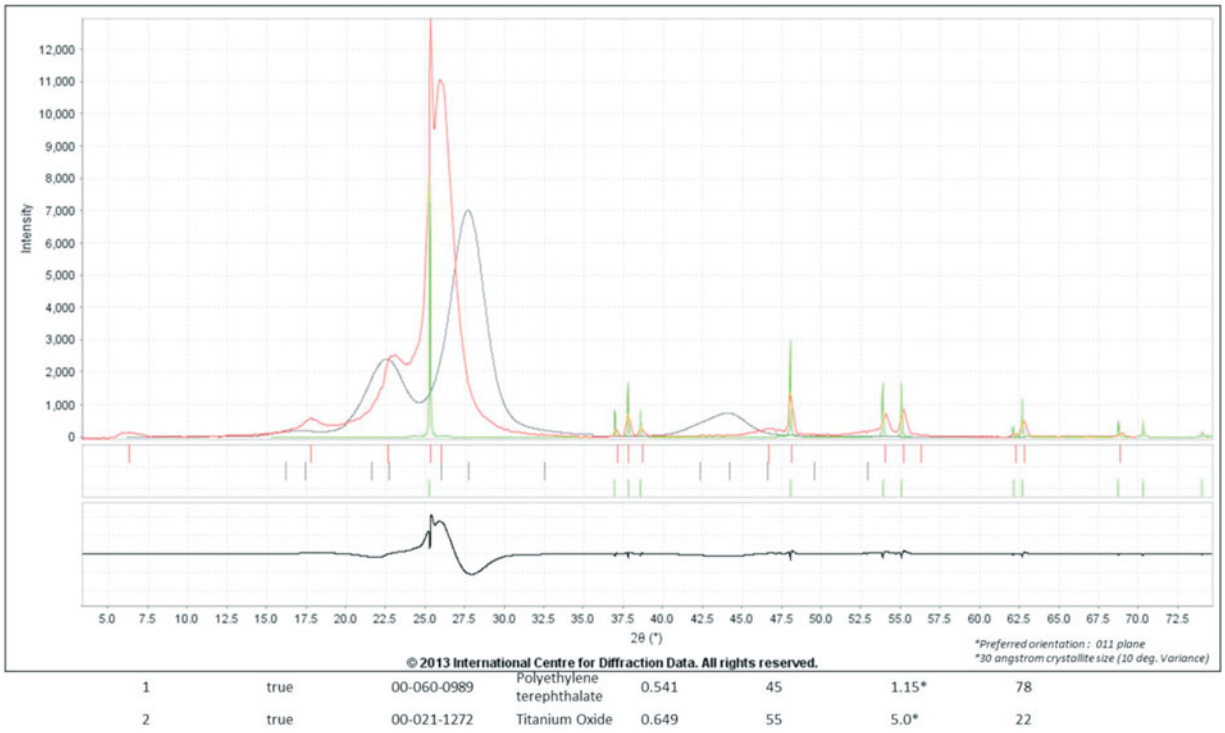


Figure 5. Best match results from a standard S/M process carried out in Sieve+. The best matched phase, thermally processed semi-crystalline PET, PDF 00-060-0989 (gray), underwent several manipulations to account for preferred orientation and peak broadening. (Color online)

particular processing steps may affect their polymer or composite before they carry out their study. Much of the structural and processing information could easily be lost or possibly misrepresented, if polymers were represented in the database using the standard d-spacings and peak intensities (d-I list) method only; especially for amorphous and semi-crystalline polymers.

B. Similarity index

Typically, PDF entries of crystalline materials are identified using comparisons of a list of d-spacings and peak intensities (d-I list). However, the lack of ordering that occurs in many of the polymers makes it difficult to accurately define an amorphous or semi-crystalline polymer using a simple

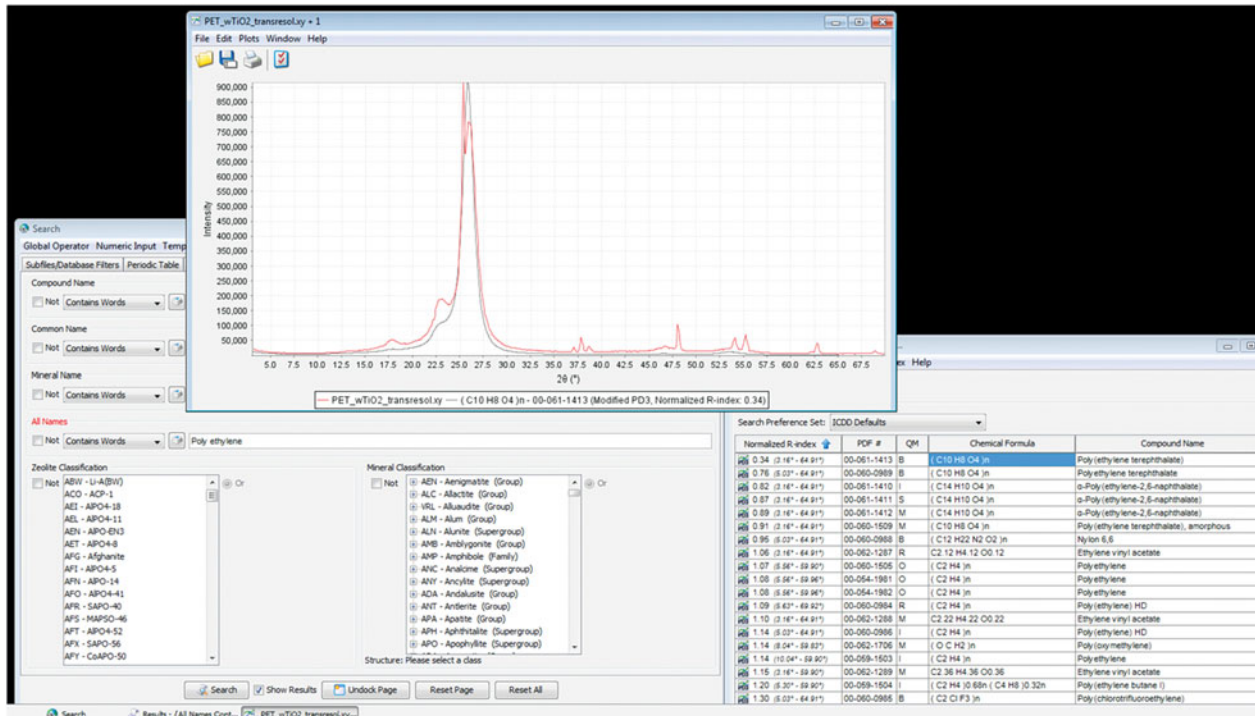


Figure 6. Results from similarity indexing in PDF-4+. (a) The experimental data (red) of a TiO₂ containing PET film. A biaxially oriented semi-crystalline phase of PET, PDF 00-061-1413 (gray), was identified as the most “similar” pattern in PDF-4+ after completion of a point-by-point comparison of the data. (Color online)

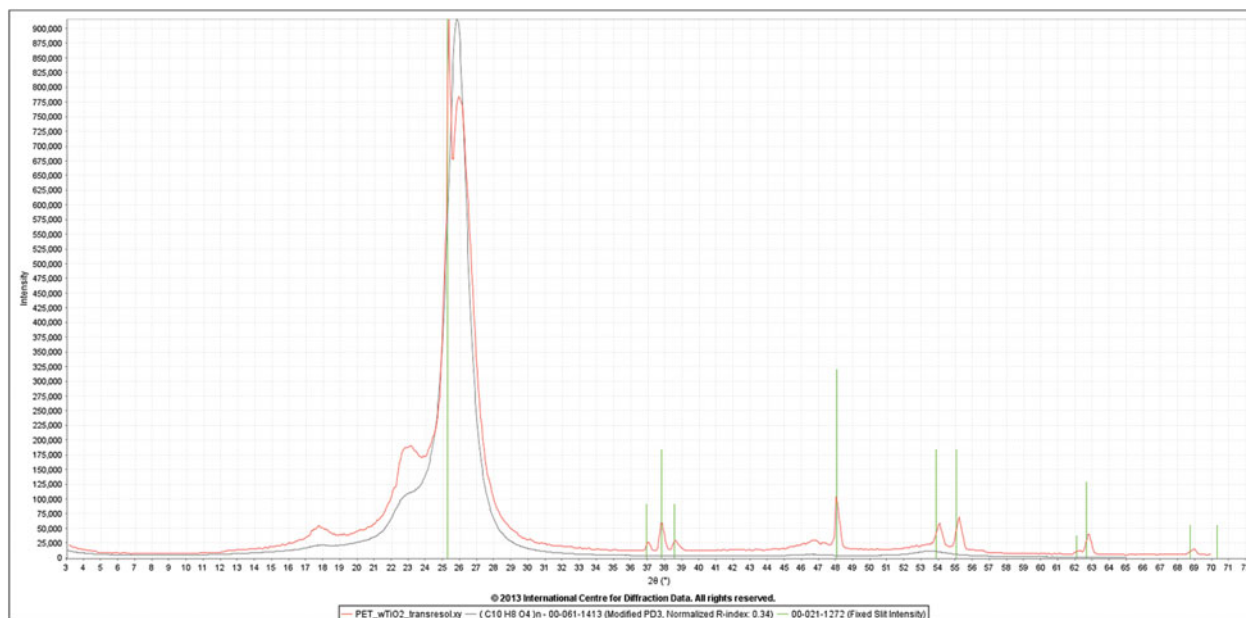


Figure 7. Experimental data (red) for TiO_2 containing PET film after identification of the polymer component (gray) via similarity indexing, and anatase (green) from standard S/M. (Color online)

d-I list; thus, requiring a different form of comparison during phase identification.

Similarity indexes are the PDF-4 tool developed to allow users to perform full pattern search/matching. In this process, digital patterns stored in the database are compared data point by data point to a user's experimental data. This process provides increased accuracy when performing S/M processes on semi-crystalline and amorphous materials.

Figure 5 illustrates results from Sieve+ (ICDD search/match software) for a standard S/M based on comparison between d-I lists only. With some extra attention to detail, both components (PET and TiO_2) were found in the Sieve+ results. However, based exclusively on d-I list comparison; the assigned compounds were not identified as the best matches. There are some noticeable differences between the PET phases that caused the goodness of the match to be penalized, and dropped to a lower ranking in the match list. Unfortunately, if not for additional chemical knowledge, this material could be easily misclassified based on d-I comparisons alone.

Using similarity indexes for materials with amorphous components can greatly enhance the accuracy of the S/M or phase identification process. A full pattern similarity search was executed using the same experimental data from the previous study, and digital patterns stored in the PDF. The results from the similarity indexing (Figure 6) revealed a higher quality match (PDF 00-061-1413, biaxially oriented PET) than what was found during the standard Sieve S/M process (PDF 00-60-0989, thermally crystallized PET). This result strongly suggests that when amorphous or semi-crystalline materials are being analyzed using PDF-4 tools, it is preferable

to carry out similarity indexing in order to improve the accuracy of your phase identification.

Once the polymer component was properly identified, the remaining peaks were matched to a TiO_2 (anatase) phase using a standard S/M process (Figure 7). This example shows the benefit of having both S/M tools (similarity indexing and standard d-I comparisons) available in the PDF-4.

IV. CONCLUSION

The addition of polymer reference patterns in the PDF continues, and will contribute to various changes to the database over time. As the understanding and use of this new sub-file increases, more polymeric entries will be added and ideally more viable information about polymers. One near future venture is the inclusion of two-dimensional XRD patterns to provide users with more information about orientation effects, and fabrication processes. This supporting data will provide increased value about the structural aspects of a compound. With time, development of new tools to extract this structural information may also inspire additional upgrades and updates to the PDF.

Alexander, L. E. (1969). *X-ray Diffraction Methods in Polymer Science* (Wiley-Interscience, New York), p. 582.

ICDD (2012). International Centre for Diffraction Data, "Public Report 2012", p. 2. The report is also available at <http://www.icdd.com>.

ICDD (2013). PDF-4+ 2013 (Database), edited by Dr. Soorya Kabekkodu (International Centre for Diffraction Data, Newtown Square, PA, USA).

Turley, J. (1965). *X-ray Diffraction Patterns of Polymers* (JCPDS-International Centre for Diffraction Data, Newtown Square, PA), p. 78.