thermo scientific

APPLICATION NOTE

AN41122

XRD investigation of three types of polyethylene films with ARL EQUINOX 100 X-ray Diffractometer

Author: Gregory Schmidt, XRD Applications Scientist

Introduction

Polyethylene (PE) is the most common plastic in use today. In 2017 alone, over 100 million tons of PE resin were produced for use primarily in the packaging market. PE accounts for roughly 34% of all plastic made in the world. While there are many variants of PE produced today, this paper studies films composed of three of the more common variants: High Density Polyethylene (HDPE), Low-Density Polyethylene (LDPE) and Linear Low-Density Polyethylene (LLDPE). While HDPE is crystalline enough to characterize further, this paper focuses on the capabilities of benchtop X-ray diffraction (XRD) to analyze the % crystallinity and crystallite size of the films.

XRD has long been considered a gold standard method for material analysis. Due to the bonding nature of plastics, XRD can perform various analyses from phase identification and quantification (for medium to highly crystalline plastics) to determination of % crystallinity and crystallite size (for less crystalline materials). The latter of these analysis types is currently the industry standard use of XRD in plastics and polymers.

Figure 1: ARL EQUINOX 100 X-ray Diffractometer.

Instrument

The Thermo Scientific™ ARL™ EQUINOX 100 X-ray Diffractometer employs a custom-designed Cu (50 W) or Co (15 W) micro-focus tube with mirror optics. Such a low wattage system does not require external water chiller or other peripheral infrastructure, allowing the instrument to be easily transported from the laboratory to the field or between laboratories.

The ARL EQUINOX 100 X-ray Diffractometer (c.f. Figure 1) provides very fast data collection times compared to other conventional diffractometers thanks to its unique curved position sensitive detector (CPS) that measures all diffraction peaks simultaneously and in real time. It is therefore well suited for both reflection and transmission measurements.

ThermoFisher SCIENTIFIC

Experimental

Two samples of each film were prepared by encasing in a windowed cardboard frame, allowing sufficient access to the film while keeping it taught and free of surface variations. The sample containers were placed in the standard stationary holder (Figure 2), in reflection orientation, with the center of each sample centered in the beam path. The samples were analyzed from 0-115° 2θ under Co Kα (1.78897 Å) radiation for 1 minute. Raw data evaluation was performed with I_MAD. Data processing, consisting of whole pattern fitting Rietveld refinement (WPF) was performed using MDI JADE 2010 equipped with the ICDD PDF – 4+. The raw XRD data for each sample was imported into MDI JADE 2010 where search/match confirmed that the material was polyethylene.

Figure 2: Standard stationary sample holder.

Results

The raw XRD data for each sample was imported into MDI JADE 2010 where search/match confirmed that the material was polyethylene. The data for each series (B and C) were refined using the WPF Rietveld analysis to provide the data presented in Figures 3 and 4. A representative report is shown in Figure 5 with the parameters of interest: %amorphous, % crystalline, crystallite size, R-factor and Goodness of Fit (R/E) presented in Table 1.

HDPE FILMS					
Sample	WT % Crystalline	WT % Amorphous	Crystallite Size (Å)	Rw	R/E (GooF)
B	90.5	9.5	198	14.24	1.18
C	87.1	12.9	307	13.18	1.38

LDPE FILMS					
Sample	WT % Crystalline	WT % Amorphous	Crystallite Size (Å)	Rw	R/E (GooF)
B	52.3	47.7	162	13.85	1.26
C	55.4	44.6	138	12.41	1.13

LLDPE FILMS					
Sample	WT % Crystalline	WT % Amorphous	Crystallite Size (Å)	Rw	R/E (GooF)
B	0	100	181	11.89	1.11
C	0.2	99.8	33	12.68	1.13

Table 1: Percent crystallinity analysis results.

HDPE is defined by a density of greater than or equal to 0.941 g/cm^3. With a low degree of branching, the mostly linear molecules exhibit well-ordered packing, maximizing intermolecular forces compared to highly branched polymers. With a high tensile strength, it is often used in products such as milk jugs, detergent bottles, butter tubs, garbage containers, and water pipes.[1] WPF analysis performed indicated a material density of 0.95 g/cm^3.

LDPE is defined by a density range of 0.910–0.940 g/cm^3. It has a high degree of short- and long-chain branching, thus the chains do not exhibit well-defined packing within the crystal structure. This results in weaker intermolecular forces compared to HDPE as the induced dipole attraction is less. The material therefore is characterized as having a lower tensile strength and increased ductility. LDPE is utilized in both rigid container and plastic film applications such as plastic bags and film wrap.[2] WPF analysis performed indicated a material density of 0.93 g/cm^3.

LLDPE is defined by a density range of 0.915–0.925 g/cm^3. LLDPE has higher tensile strength than LDPE due to its substantially linear polymeric structure with extensive short branches, therefore exhibiting higher impact and puncture resistance than LDPE. It is commonly used in packaging, particularly film for bags and sheets as well as: cable coverings, toys, lids, buckets, containers, and pipes.[3] WPF analysis performed indicated a material density of 0.92 g/cm^3.

Percent crystallinity analyses were performed on all PE samples, yielding the values and R-factors. The results are summarized in Table 1. As expected, the HDPE samples are predominantly in their crystalline form. The LDPE and LLDPE films, however, exhibit a reversed trend in % crystallinity compared to their pellet forms. In pelletized form, LLDPE usually has a slightly higher % crystallinity than LDPE. It is postulated that this film is oriented along the long polymeric structure with the orthogonal short chains in the horizontal plain to the beam, therefore coherent diffraction was not observed from these side chains.

Figure 3: A) HDPE B) LDPE and C) LLDPE B series films refined and fit data.

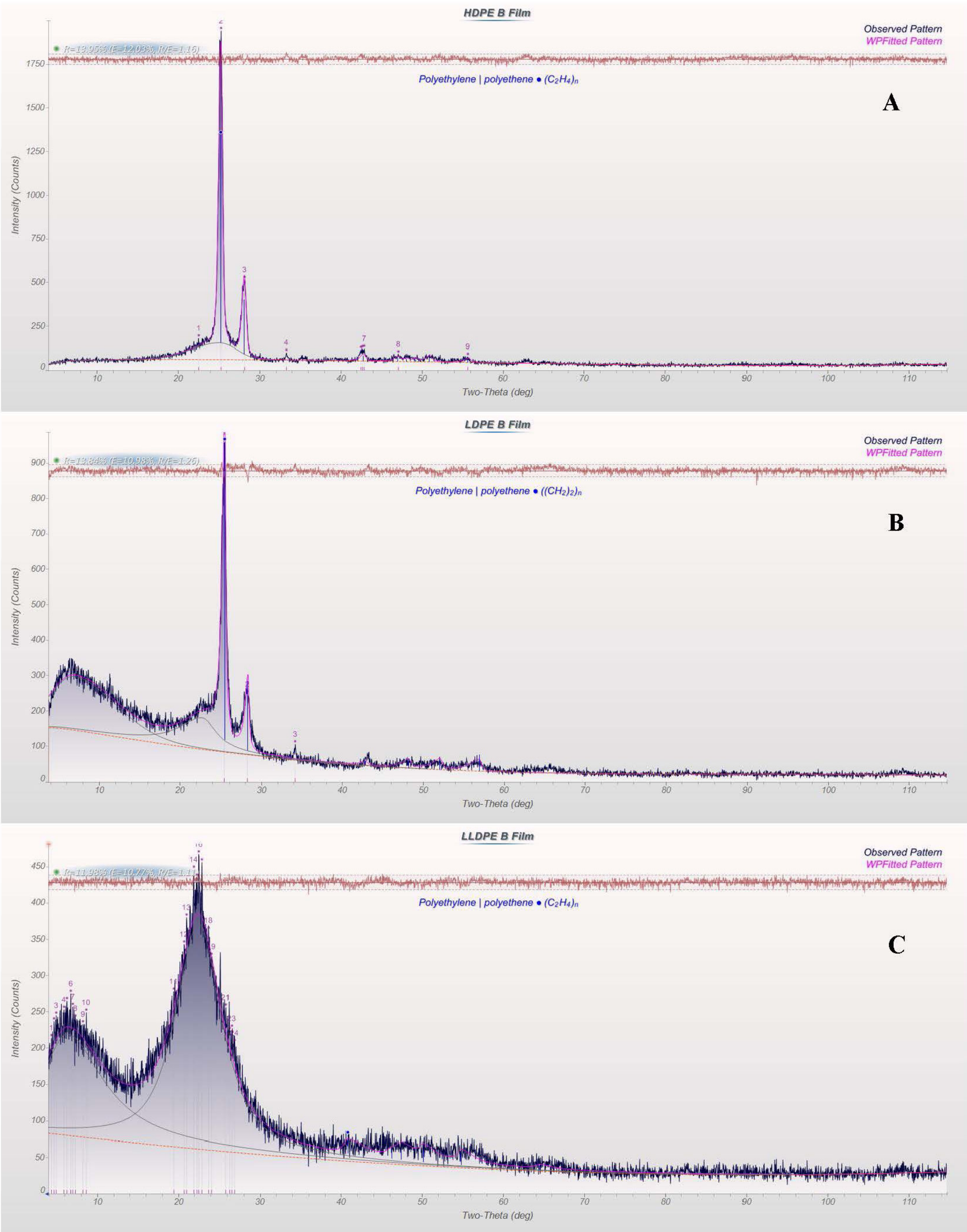


Figure 4: A) HDPE B) LDPE and C) LLDPE C series films refined and fit data.

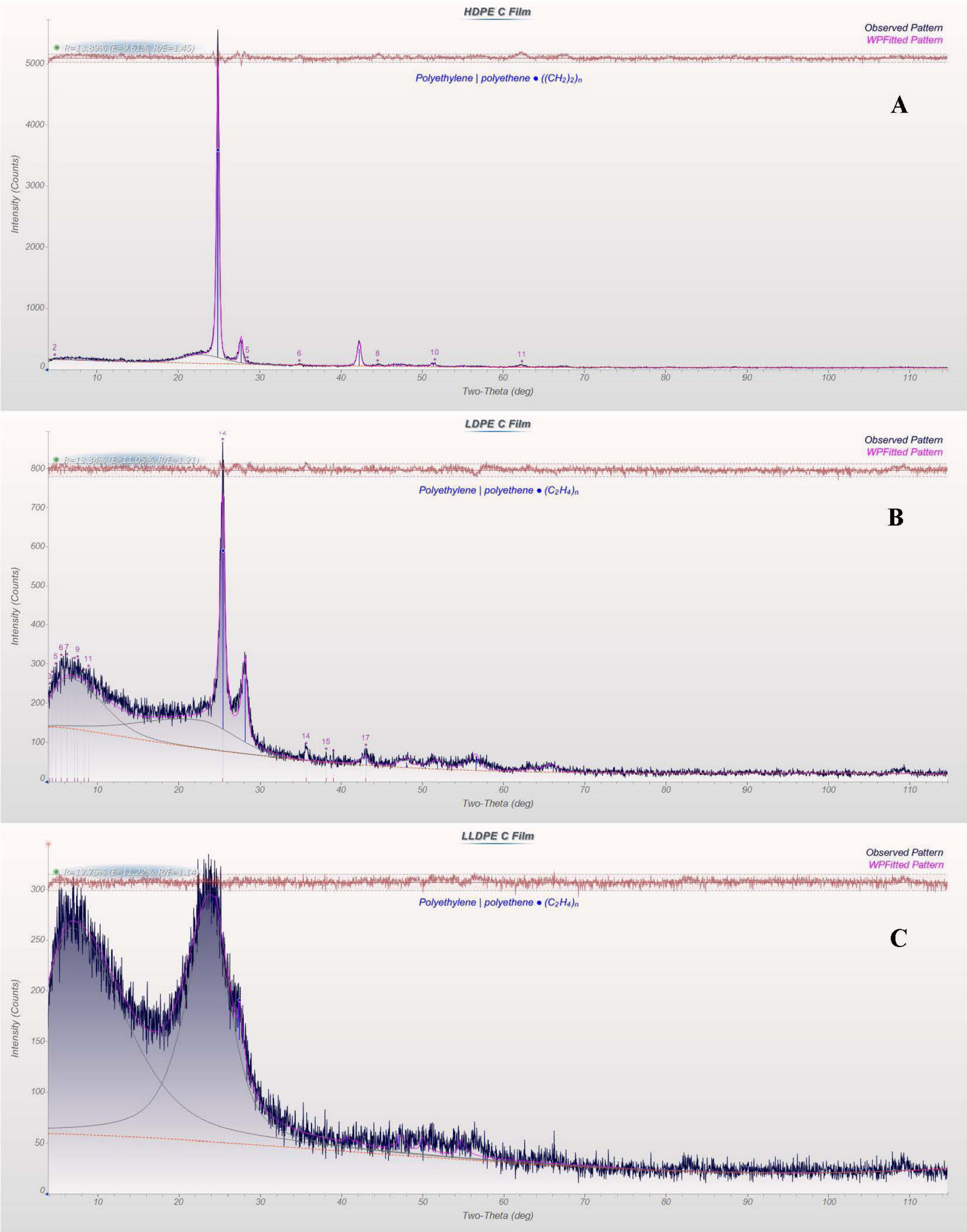
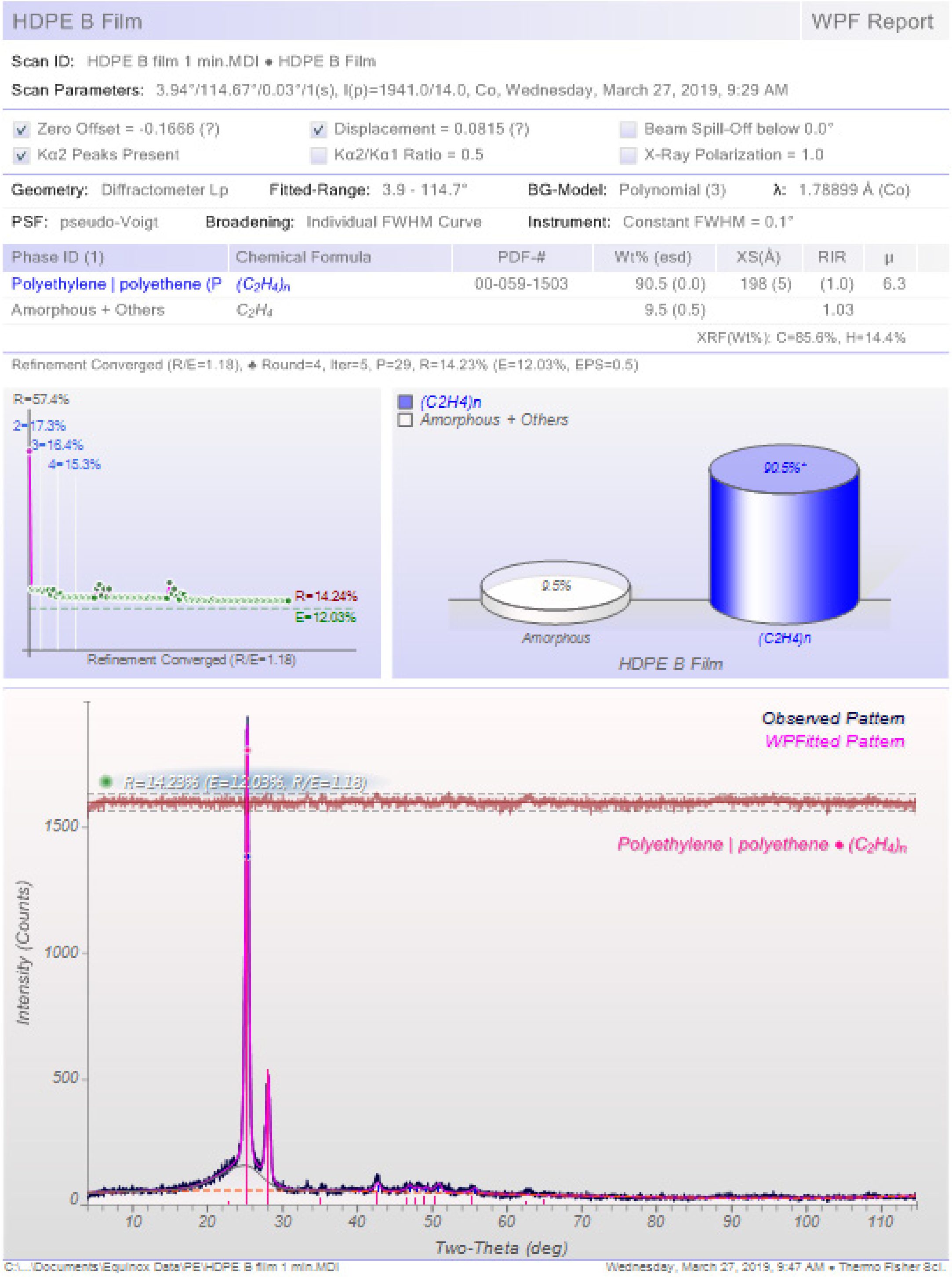


Figure 5: Representative report generated for HDPE B Film WPF refinement.



thermo scientific

Conclusion

The resolution and speed of the ARL EQUINOX 100 X-ray Diffractometer enables the ability to fully analyze phase and % crystallinity properties of plastics and polymers. A 1-minute measurement time was chosen to highlight such capabilities. Therefore, the ARL EQUINOX 100 benchtop X-ray Diffractometer is an ideal choice for the analysis of the crystalline nature of plastics and polymers.

References

[1] *"Market Study: Polyethylene – HDPE".*
Ceresana Research. May 2012.

[2] *"Market Study: Polyethylene – LDPE (2nd edition)".*
Ceresana. October 2014.

[3] *"Market Study: Polyethylene – LLDPE 2nd. edition".*
Ceresana. November 2014.

Find out more at **thermofisher.com/xrd**

ThermoFisher SCIENTIFIC