

# Validation of Crystallinity Measurements of Medical Grade PEEK Using Specular Reflectance FTIR-microscopy

+<sup>1</sup>Jaekel, D J; <sup>1</sup>Medel, F, J; <sup>1,2</sup>Kurtz, S M

+<sup>1</sup>Drexel University, Philadelphia, PA; <sup>2</sup>Exponent, Inc., Philadelphia, PA  
smk38@drexel.edu

**Introduction:** Polyetheretherketone (PEEK) is widely used as a structural load-bearing polymer in spine implants and is increasingly used in orthopedic and trauma implants [1]. Characterizing the degree of crystallinity in PEEK is critical for evaluating the mechanical behavior of implants [1]. Wide angle X-ray scattering (WAXS) is considered the most accurate method for measuring crystallinity in PEEK [1], however it is not practical for measurement of as-manufactured PEEK implants, which can contain image contrast agents. Differential scanning calorimetry (DSC) has also been used to characterize PEEK crystallinity, but has limited accuracy due to recrystallization phenomena that occur during the experiment [1].

Specular reflectance Fourier transform infrared (FTIR) microscopy has been reported to provide accurate characterization of crystallinity in industrial, unfilled grades of PEEK [2]. The generalizability of R-FTIR to characterize crystallinity in medical grades of PEEK, containing fiber reinforcement or radiopacifiers, remains unknown. The aim of this study was to compare the utility of R-FTIR, WAXS and DSC techniques to evaluate the degree of crystallinity for a range of medical grades of PEEK. We hypothesized that specular reflectance FTIR would detect changes in crystallinity due to annealing treatments and incorporation of carbon fibers or radiopaque compounds into medical grade PEEK.

**Materials and Methods:** Three medical grade PEEK-OPTIMA resins were obtained from the manufacturer in pellet form (LT1, Opaque LT1 (RO), and LT1CA30 carbon fiber reinforced (CF30): Invibio, Ltd., UK). An unfilled industrial sample was also obtained with the same molecular weight as LT1 (450G: Victrex). Resin was heated at 150°C for at least 2 hrs to remove residual humidity prior to processing. Specimens were then injection molded into tensile dogbone specimens with a BOY 50M molder, under conditions recommended by the manufacturer. For each type of resin, four treatment-processing groups were created: as-injection molded (unannealed), 200°C annealed, 300°C annealed, and amorphous PEEK. The 200°C annealed samples were dried at 150°C for 3 hrs, and then ramp heated at 12°C/min to 200°C. They were held at 200°C for 4 hrs and then ramp cooled at the same rate to below 140°C. Annealing was performed for the 300C group in the same fashion except there was no controlled ramp heating or cooling. Amorphous PEEK was created by heating to 400°C for 30 minutes, followed by quenching in liquid nitrogen.

Three samples per processing condition (n=3) were evaluated for crystallinity using DSC and WAXS. For DSC, approximately 7 mg samples were evaluated in a Q2000 DSC apparatus (TA Instruments) and heated at 20°C/min from 23°C to 400°C. Crystallinity was calculated by linear integration of the heat flow curve from 300°C to 360°C and assuming the heat of fusion of perfectly crystalline PEEK is 130 J/g. Mass values were corrected for Radio Opaque and CFR-PEEK specimens, since they consisted of only 80% and 70% polymer respectively. WAXS scans were performed with a Siemens D500 X-ray diffractometer. Diffraction patterns were acquired at a scanning rate of 0.03°(2θ)/min over an angular range of 5°<2θ<45°.

Specular reflectance FTIR measurements were collected with a Nicolet Continuum (Thermo Electron Corp.) with an aperture size of 360 μm x 360 μm. FTIR spectra were acquired at a resolution of 4cm<sup>-1</sup> at 100 scans per spectrum. The Kramers-Kronig transform algorithm was used to derive the absorbance spectra. In the spectra range of 1400cm<sup>-1</sup> to 900cm<sup>-1</sup>, an automatic baseline correction was applied, and a baseline for the height measurements was derived from the zero value absorbance points on the spectra. As previously established, the height ratio of the peaks on the absorption bands at 1305cm<sup>-1</sup> and 1280cm<sup>-1</sup> was recorded for each material group, since these peaks are known to be sensitive to crystallinity [2] (Figures 1 & 2). The ratio of these peaks defines the crystallinity index (CI) for FTIR (Figure 1).

**Results:** FTIR spectra displayed similar trends for the four processing conditions, with amorphous material displaying consistently the lowest CI values and 300°C material the highest CI. A highly linear correlation was observed between CI and crystallinity determined by WAXS for OPTIMA-LT1 (r<sup>2</sup> = 0.98, Figure 3). A similar correlation between CI and crystallinity was observed for the unfilled industrial grade (r<sup>2</sup> = 0.98). With the CF grade, crystallinity increased from 14.17% ± 0.39% to 16.80% ± 0.91%, and 21.98% ± 0.68% from

molded to 300°C annealed samples, respectively. WAXS patterns for RO had dramatically different patterns with respect to other PEEK materials, and the method to calculate crystallinities could not be applied.

In contrast with FTIR, DSC measurements were insensitive to changes in processing. For LT1, DSC provided indistinguishable crystallinity values (28.5%±1.2%) regardless of annealing treatments, the only exception being amorphous PEEK samples (18.0%±1.7%). DSC crystallinities measured in CF samples varied from 32.0% ± 2.2% for all conditions except amorphous (0%). For RO, DSC values were 15.0%±2.2% (Amorphous), 29.4%±1.0% (Inject. Mold.), 30.9%±1.0% (200°C Annealed), and 37.6% ± 0.4% (300°C).

**Discussion:** The results of this study establish specular reflectance FTIR as a suitable technique for characterizing crystallinity of PEEK biomaterials. In contrast with WAXS and DSC, FTIR provided consistent trends in crystallinity as a function of well-understood processing techniques. Although WAXS proved to be suitable for characterizing unfilled PEEK grades, diffraction patterns of PEEK composites were altered due to X-Ray scattering of carbon fibers and barium sulfate. In these cases, more complicated methods involving peak deconvolution and fitting are needed to calculate crystallinities. Moreover, DSC methods were unable to distinguish between PEEK materials of varying crystallinity. These findings will provide a useful basis for developing a standard method for characterizing crystallinity in medical grade PEEK under the auspices of ASTM.

**References:** [1] Kurtz and Devine, *Biomaterials* 2007; [2] Chalmers et al, *The Analyst* 1998.

**Acknowledgement:** Special thanks to Invibio, Inc.

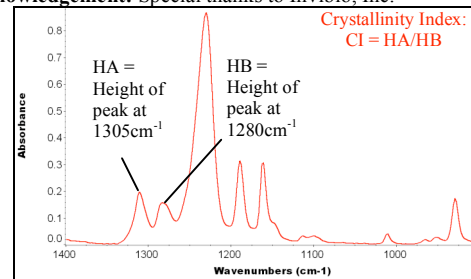


Figure 1: Typical specular reflectance spectra with defined peaks

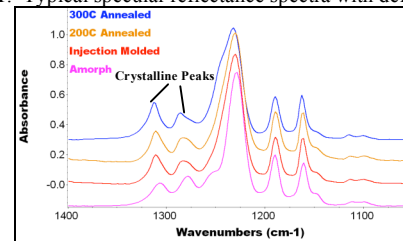


Figure 2: FTIR specular reflectance spectra from OPTIMA LT1

	OPTIMA -LT1	OPTIMA - Radio Opaque	OPTIMA - Carbon Fiber	Victrex 450G
Amorphous	0.81 ± 0.01	0.80 ± 0.02	0.76 ± 0.04	0.76 ± 0.01
Injection Molded	1.23 ± 0.02	1.25 ± 0.04	1.12 ± 0.06	1.18 ± 0.07
200C	1.27 ± 0.03	1.32 ± 0.06	1.23 ± 0.09	1.27 ± 0.02
300C	1.42 ± 0.04	1.48 ± 0.03	1.34 ± 0.09	1.50 ± 0.02

Table 1: Summary of Crystallinity Index (Mean ± SD) Results

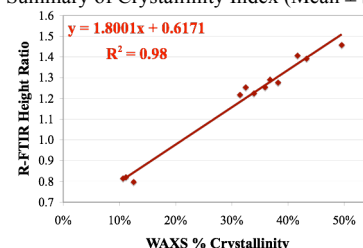


Figure 3: Correlation of R-FTIR Measurements for OPTIMA LT1