New Technique for Crystallinity Measurements of Medical Grade PEEK Utilizing FTIR-microscopy

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Introduction: Polyetheretherketone (PEEK) is widely used as a structural load-bearing polymer in spine implants and is increasingly used in orthopedic and trauma devices [1]. Characterizing the degree of crystallinity is critical for predicting the mechanical behavior of PEEK 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 (R-FTIR) microscopy has been reported to provide accurate characterization of crystallinity in industrial 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 R-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 (Invibio, Ltd., UK) resins LT1, radiopaque LT1 (RO), and carbon fiber reinforced (CFR), as well as an unfilled industrial grade, 450G (Victrex, UK), with the same molecular weight as LT1, were obtained from the manufacturer in pellet form. Specimens were then injection molded following manufacturer recommendations. For each type of resin, four treatment-processing groups were created: as-molded, 200°C annealed, 300°C annealed, and amorphous. 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 140°C. Annealing was performed for the 300°C group in the same fashion except there was no controlled ramp heating or cooling. Amorphous PEEK was heated to 400°C for 30 min., followed by quenching in liquid nitrogen.

Five samples per processing condition (n=5) 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. 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 $5° < 2\theta < 45°$.

R-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^{-1} at 100 scans per spectrum. The Kramers-Kronig transform algorithm was used to derive the absorbance spectra. In the spectra range of 1400cm-1 to 900cm-1, 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^{-1} and 1280cm^{-1} was recorded for each material group, since these peaks are known to be sensitive to crystallinity [2] (Figure 1). The height ratio of these peaks served to define a crystallinity index (CI) for R-FTIR (Figure 1).

Results: As-molded PEEK materials displayed similar R-FTIR CIs (~ 1.25), regardless of the addition of fillers. All annealed PEEK materials exhibited increased CIs with the highest increase registered after annealing at 300 ºC (CI: 1.35-1.51). Also, all the amorphous materials consistently displayed the lowest CI values (~0.8). Percent crystallinity results calculated from WAXS measurements confirmed the trends found in the R-FTIR study. With the CFR grade, WAXS crystallinity increased from 25.4% to 41.4% after annealing of the as-molded CFR specimens at 300°C. All the amorphous samples for CFR and RO had no distinguishable crystalline peak signals in the WAXS patterns, so the calculated values were essentially zero. WAXS patterns for RO were dramatically different with respect to other PEEK grades, and curve-fitting became more complex and time intensive. A highly linear correlation was observed between CI and crystallinity determined by WAXS for LT1 and 450G ($R2 = 0.98$, Figure 2).

In contrast with R-FTIR, DSC measurements were less sensitive to changes in crystallinity. For 450G, DSC provided indistinguishable crystallinity values (27.5%±0.6%) regardless of annealing treatments with the only exception being 300°C samples (37.2%±2.4%). For LT1, the crystallinity value for 300°C annealed were lower than those for as-molded and 200°C annealed. In general, percent crystallinity fluctuated closely to 30%.

Discussion: The results of this study establish R-FTIR as a suitable technique for characterizing crystallinity of PEEK biomaterials. In contrast with DSC, R-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 time intensive curve-fitting procedures were 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, *Biomaterals* 2007; [2] Chalmers et al, *The Analyst* 1998.

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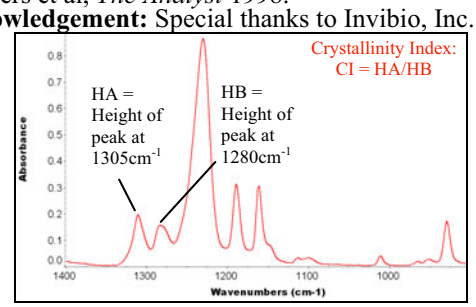

Figure 1: Typical R-FTIR spectra with defined peaks

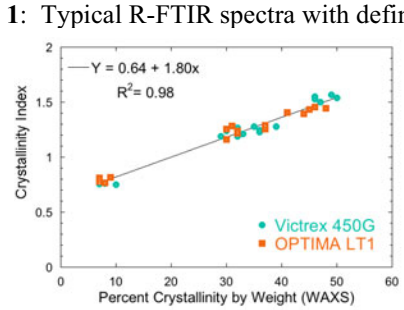

Figure 2: Correlation of R-FTIR Measurements and WAXS for LT1 and 450G