Production and Characterization of Melt-Spun Poly(Ether Ether Ketone) Fibers for Biomedical Applications

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Statement of Purpose: Poly(Ether Ether Ketone) (PEEK) is gaining popularity in biomaterials applications, and in the orthopedic community in particular. This is largely due to PEEK's superior mechanical properties and good biocompatibility. To date, these studies have focused primarily on the use of injection-molded parts of either neat PEEK or various carbon fiber-reinforced composites[1]. In contrast, there is little work reporting on the potential of PEEK fibers for applications in the realm of biomaterials. Indeed, there are distinct advantages to spinning many polymers into fibers. The purpose of this work is to characterize the effect of fiber processing, relative molecular weight, and post-processing heated solid-state drawing on the mechanical, structural, and thermal properties of melt-spun PEEK fibers. Additionally, the potential use of PEEK fibers for biomaterials applications is assessed based on the findings of this study.

Methods: PEEK fibers were spun at draw-down ratios (DDR) of 100 and 200 (and thus, two resulting diameters) from two separate PEEK grades: Victrex 150G (Victrex, PA) and Evonik 4000G (Evonik, Germany). Draw-down ratio is defined as the ratio of the take-up velocity to the extrusion velocity, as shown in equation 1.

$$DDR = \frac{V_e}{V_t} \quad \text{(eq. 1)}$$

These are of a relatively low and high molecular weight, respectively. Fibers were then left as-spun, or subjected to either an annealing step at 280°C for 90 minutes, or subjected to a heated post-drawing step at 280°C and a post-draw ratio (DR) of 2 (except for fibers of DDR=200 prepared from grade 4000G, which resulted in DR=1.5), where DR is defined as follows:

$$DR = \frac{\Delta l}{l_0} + 1 \quad \text{(eq. 2)}$$

Sample groups were then analyzed for differences in structural and thermal characteristics via Wide Angle X-ray Scattering (WAXS) (Rigaku, Japan) and differential scanning calorimetry (Perkin-Elmer, CT). Fibers were imaged with scanning electron microscopy to evaluate morphology and diameter (JEOL 5600, Japan). Additionally, fibers were tested in tension at a strain rate of 0.2 /min to assess changes in mechanical properties as a function of processing condition (Linkam, England). Three-way ANOVA with Student-Neuman-Keuls post-hoc analysis was performed on mechanical data to determine statistically significant differences in properties within and between sample groups.

Results: DSC results for fibers from 4000G fibers show a much higher T_m (347°C) than bulk samples (335°C), as-spun or annealed fibers (~340°C). Fibers from the low molecular weight Victrex 150G grade show a consistent T_m at 345°C, regardless of whether a bulk sample or fiber of any treatment group, suggesting that structurally, there may not be the same degree of chain extension in this fiber. Data taken from WAXS shows that 150G fibers increase in crystallinity for both annealing and hot drawing (35% and 30%, respectively) compared to an amorphous as-spun sample. The same is true for 4000G samples, although as-spun samples show initial crystallinity of 5% and 15%. Average crystal size is highest for annealed samples (approximately 130Å) while unchanged between as-spun and drawn samples (approximately 90Å). Qualitatively, drawn samples show significant increases in crystal orientation, as to be expected (see Figure 1).

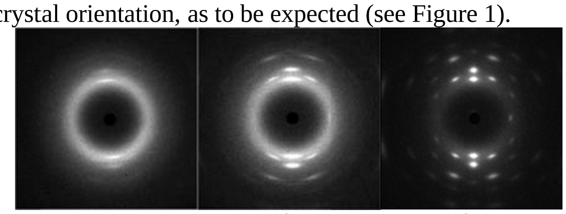

Figure 1: WAXS patterns, 4000G fibers, DDR=100. Left to Right: as-spun, annealed, hot-drawn.

Tensile testing reveals that the most dramatic increase in strength over bulk PEEK(up to ~550 MPa from 100 MPa) and modulus (up to 6.5 GPa from 3.9 GPa), and most dramatic decrease in ductility is found in highly drawn samples, regardless of draw down ratio or molecular weight. 4000G fibers showed higher average strength than 150G, and hot drawing showed the most significant increase in strength regardless of molecular weight grade or draw-down ratio as shown in figure 2 ($p<0.05$).

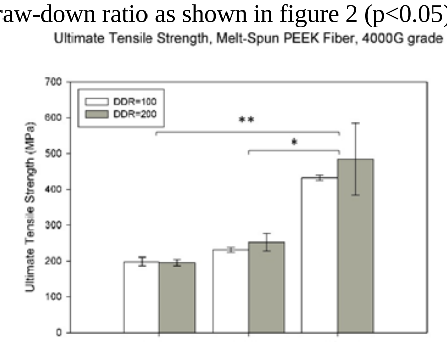

Figure 2: Ultimate tensile strength of PEEK fibers (avg. ±SD). *, ** denotes significant difference between treatments ($p<0.05$). Differences between treatment type regardless of DDR are considered here.

Conclusions: PEEK fibers produced with additional post-drawing have shown the highest strength of fibers tested. Additionally, WAXS patterns show increase in crystallinity for annealing and drawing, with increased orientation for hot drawn samples. These results imply that properties of the material could be "tuned" to meet a range of desired needs while utilizing a material already popular in the biomaterials community. Highly drawn fibers might find use in artificial ligament design or as reinforcement for composite materials for orthopedic use. Future work should include further development of novel applications to take advantage of the properties demonstrated here.

References:

1. Kurtz, Steven M. *PEEK Biomaterials in Trauma, Orthopedic, and Spinal Implants.* Biomaterials, 28;32. 2007.

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