Effects of Annealing on Hydroxyapatite Whisker Reinforced Polyetherketoneketone Scaffolds

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Introduction: Polyetherketoneketone (PEKK) scaffolds reinforced with hydroxyapatite (HA) whiskers have been designed to (1) exhibit mechanical properties that are similar to that of human trabecular bone and (2) promote bioactivity by HA crystals exposed on the scaffold surfaces.[1,2] While the above studies investigated as-molded scaffolds, dense PEEK reinforced with HA was previously reported to exhibit improved strength after a subsequent annealing treatment.[3] Therefore, the objective of this study was to investigate the effects of a post-molding annealing treatment on the mechanical properties of HA whisker reinforced PEKK scaffolds.

Methods: HA whiskers were synthesized using the chelate decomposition method and exhibited a mean length of ~20 μm, mean width of ~3 μm, and mean aspect ratio of ~8, as described else in detail elsewhere.[1-5] PEKK powder with a mean size of ~70 μm was used as-received (Oxford, OXPEKK-C).

PEKK composite scaffolds with 20 vol% HA whisker reinforcement and 75 vol% porosity were prepared by co-dispersing appropriate amounts of HA whiskers and PEKK powder in ethanol using ultrasonication. The appropriate amount of a NaCl porogen was hand-stirred into the suspensions. The powder mixture was collected by vacuum filtration, dried overnight, and consolidated at 125 MPa in a cylindrical die with a diameter of 10 mm. The scaffold was then compression molded at 250 MPa and 350°C. Scaffolds were soaked in deionized water for 3 days to remove the NaCl porogen. Annealed scaffolds were heated to 200°C for 4 h and then cooled to 150°C over 4 h to allow for recrystallization of the polymer. Specimens 10 mm in height were sectioned from as-molded or annealed scaffolds.

The mechanical properties of as-molded (n = 5) and annealed scaffolds (n = 5) were evaluated in unconfined uniaxial compression at a crosshead speed of 1mm/min, as described in detail elsewhere.[1] Specimens were soaked in phosphate buffered saline (PBS) at 37°C overnight prior to testing. The compressive modulus, yield stress, and yield strain were compared using an unpaired Students' t-test with a level of significance of 0.05.

Results and Discussion: The compressive modulus of the annealed scaffolds was decreased by 18% ($p < 0.05$) compared to the as-molded scaffolds (Fig. 1a). The yield strength and yield strain of annealed scaffolds was increased by 35% ($p<0.05$) and 61% ($p<0.0005$), respectively, compared to the as-molded scaffolds (Fig. 1b and c).

Improvements in strength and ductility after annealing came with an expected sacrifice in stiffness (Fig. 1). However, the percent increase in strength and ductility were much larger than the decrease in stiffness. These trade-offs must be considered in the design of scaffolds.

The differences in mechanical properties between the as-molded and annealed scaffolds were most likely due to a change in polymer crystallinity, which can be investigated using Fourier transform infrared spectroscopy (FT-IR).[6] Moreover refinement of the annealing treatment may lead to optimized properties.

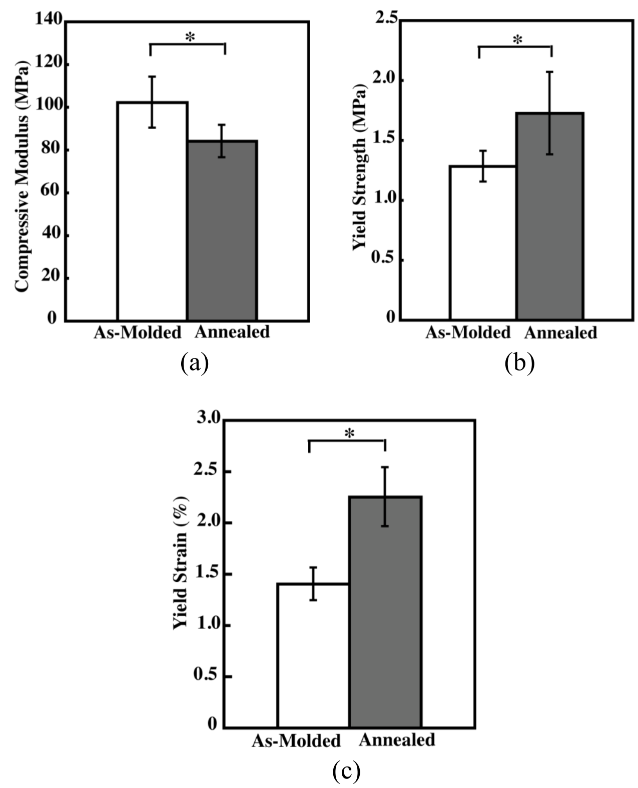

Fig. 1. The mean compressive (a) modulus, (b) yield strength, and (c) yield strain for as-molded vs. annealed HA reinforced PEKK scaffolds with 20 vol% HA whisker reinforcement and 75% porosity. Error bars show one standard deviation.

Conclusions: A post-molding annealing treatment was shown to significantly improve the strength and ductility of HA whisker reinforced PEKK scaffolds.

References: [1]Converse GL *et al.*, *J. Mech. Behav. Biomed. Mater.*, 2:627-635, 2009. [2]Converse GL *et al.*, *Acta Biomaterialia* in press. [3]Converse GL *et al.*, *Biomaterials*, 28:927-935, 2007. [4]Roeder RK *et al.*, *J. Biomed. Mater. Res.*, 67A:801-812, 2003. [5]Roeder RK *et al.*, *J. Am. Ceram. Soc.*, 89:2096-2104, 2006. [6]Jaekel DJ *et al.*, *ANTEC Conference Proceedings*, 11, 2009.