

Tensile Properties of Hydroxyapatite Whisker Reinforced Polyetheretherketone

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ABSTRACT

Polyetheretherketone (PEEK) was reinforced with 0-40 vol% hydroxyapatite (HA) whiskers using a novel powder processing and compression molding technique. A powder mixture was uniaxially pressed into a composite powder compact and compression molded into a flat composite bar using an open-channel die, such that the HA whiskers exhibited a preferred orientation along the length of the bar and tensile specimens. As expected, increased HA whisker reinforcement resulted in increased elastic modulus, but decreased ultimate tensile strength and strain- or work-to-failure. PEEK reinforced with 40 vol% HA whiskers exhibited an elastic modulus of 16-18 GPa. PEEK reinforced with 20 vol% HA whiskers had an ultimate tensile strength of 70-80 MPa. Human cortical bone exhibits an elastic modulus of 17-26 GPa and an ultimate tensile strength of 80-150 MPa in the longitudinal direction (direction of principal stress). Stiffness coefficients measured by ultrasonic wave propagation indicated a level orthotropy also similar to that of human cortical bone tissue.

INTRODUCTION

The extracellular matrix (ECM) of human bone tissue is a composite comprising a collagen matrix reinforced with 40-50 vol% apatite crystals [1,2]. The apatite crystals are plate-like and elongated with a preferred orientation in directions of principal stress, such as the longitudinal direction of long bones [1,3]. Therefore, bone tissue exhibits corresponding anisotropic mechanical properties [4].

Mechanical mismatch problems (e.g., stress shielding) exist between conventional orthopaedic biomaterials and bone tissue. Synthetic biomaterials that are 1) biocompatible, 2) bioactive and 3) able to be tailored to mimic the mechanical properties of bone tissue might be advantageous for implant fixation, synthetic bone graft substitutes, tissue engineering scaffolds, and other orthopaedic applications. To this end, biocompatible polymers have been reinforced with bioactive hydroxyapatite (HA) powder and whiskers.

The seminal work in bone-like, synthetic biocomposites was the development of HAPEXTM, a high density polyethylene (HDPE) matrix reinforced with HA powder [5]. Injection and compression molded HAPEXTM has been used clinically in non-load bearing implants. Hydrostatic extrusion was used to further improve the mechanical properties by inducing molecular orientation in the polymer [6]. More recently, HDPE was reinforced with high volume fractions of HA whiskers using a novel powder processing and compression molding technique that induced a preferred orientation of HA whiskers within the HDPE matrix [7]. HDPE reinforced with HA whiskers exhibited improved mechanical properties compared to HA powder and also possessed mechanical anisotropy similar to that found in human bone tissue [7]. However, the elastic moduli of hydrostatically extruded HAPEXTM [6] and HA whisker reinforced HDPE [7] in the longitudinal direction were only equivalent to human cortical bone in the transverse direction, and tensile strengths were insufficient for use in load-bearing implants.

Therefore, further improvements in mechanical properties were limited in part due to the use of HDPE as the matrix phase. Injection molded polyetheretherketone (PEEK) reinforced with HA powder has been recently reported to exhibit mechanical properties approaching those of human cortical bone tissue in the longitudinal direction [8,9].

The objective of this study was to investigate whether HA whisker reinforced PEEK could mimic the mechanical properties and anisotropy of human bone ECM. PEEK was reinforced with 0-40 vol% HA whiskers using a novel powder processing and compression molding technique adapted from our previous work with HA whisker reinforced HDPE [7]. Tensile properties and stiffness coefficients were measured and compared to human cortical bone tissue, as a benchmark.

EXPERIMENTAL METHODS

Composite Processing

Composites were produced containing 0, 20 and 40 vol% HA whisker reinforcements. HA whiskers were hydrothermally synthesized at 200°C using methods described previously [7,10]. The as-synthesized HA whiskers were measured to have a length of $28.7 \pm 15.6 \mu\text{m}$, a width of $3.0 \pm 0.9 \mu\text{m}$, and an aspect ratio of 9.9 ± 5.5 (mean \pm standard deviation). Appropriate amounts of a commercially available PEEK powder (150XF, Victrex plc) and the as-synthesized HA whiskers were ultrasonically co-dispersed in ethanol and consolidated using vacuum filtration. The powder mixture was dried overnight in an oven at 90°C and uniaxially pressed at 32 MPa using a hydraulic platen press. The resulting composite powder compact was placed in the center of an open-channel die and compression molded into a $2.6 \times 10 \times 125$ mm composite bar. The die and powder compact were pre-heated to 345-350°C in a vacuum oven and transferred to an automated, hydraulic platen press (G30H-15-CPX, Wabash) for compression molding. During molding, the composite mixture of HA whiskers and PEEK was extruded towards the open ends of the channel die, and pressure was applied as the polymer solidified. The composite bar was removed before the die cooled to room temperature in order to mitigate thermal stresses and cracking. ASTM D638 type V tensile specimens were machined from composite bars such that the tensile axis of each specimen corresponded to the direction of flow during compression molding. Machined tensile specimens were tested either as-molded or were first annealed in a forced convection oven by heating to 200°C, holding 4 h and cooling to 150°C in 4 h.

Mechanical Testing

Uniaxial tensile tests were performed in accordance with ASTM D638, with a crosshead speed of 1 mm/min, using an electromagnetic test instrument (ELF 3300, Endura TEC). Force-displacement data was used to calculate the elastic modulus (E), ultimate tensile strength (UTS), strain-to-failure (ϵ_f) and work-to-failure (w_f). The fracture surface of tensile specimens was examined using a scanning electron microscope (SEM) (Evo 50, LEO Electron Microscopy).

The elastic anisotropy of annealed composites was characterized by measuring stiffness coefficients in the three orthogonal specimen directions (C_{ii}) using an ultrasonic wave propagation technique described in detail elsewhere [11,12]. Annealed composite bars were sectioned into specimens with nominal dimensions of $2.6 \times 10 \times 10$ mm. Dilational ultrasonic waves were transmitted to and received from the specimen using 2.25 MHz transducers (Model 5800, V106RM, Panametrics). The time required for the wave to propagate through the specimen was monitored using an oscilloscope (TDS-1000, Tektronix). The stiffness coefficient

was calculated as the square of the wave velocity in a given specimen direction multiplied by the measured bulk density of the specimen. The bulk density of each individual specimen was measured using Archimedes' principle.

One-way ANOVA (JMP 5.1, SAS Institute, Inc.) was used to compare measured mechanical properties between experimental groups. Post-hoc comparisons were performed using a Student's T-test. The level of significance was 0.05.

RESULTS AND DISCUSSION

HA whisker reinforced PEEK composites were reliably produced with 0, 20 and 40 vol% reinforcement using mold temperatures in the range of 345-350°C. The optimal mold temperature increased, within that range, as the level of HA whisker reinforcement increased. Material or manufacturing defects occurred in composites compression molded at temperatures above or below the optimum for a given reinforcement level. Composites molded at lower temperature generally cracked or solidified before reaching the desired thickness. Areas of unmelted composite powder were visible in extreme cases. At the other extreme, surface oxidation was evident in composites compression molded above 350°C. In such cases, the composite bar typically adhered to the mold surface. Finally, the tensile properties of as-molded composites exhibited substantial inter-specimen variability, which was decreased using the annealing treatment described above (Table I).

As expected, tensile tests showed that increased HA whisker reinforcement resulted in increased elastic modulus, but decreased ultimate tensile strength, strain-to-failure and work-to-failure (Table I, Fig. 1). PEEK reinforced with 40 vol% HA whiskers exhibited an elastic modulus of 16-18 GPa for as-molded and annealed specimens, which is within the range of 17-26 GPa typically reported for human cortical bone in the longitudinal direction [1,11,13,14]. Also as expected, the use of PEEK as the matrix phase resulted in a significantly higher elastic modulus than for previous work using HDPE [7] (Fig. 3). Note that these results were achieved using HA reinforcement levels similar to those found in bone tissue [1,2]. PEEK reinforced with HA whiskers also resulted in higher elastic moduli at equal levels of reinforcement compared to a previous study using an equiaxed HA powder [8,9].

HA whisker reinforced PEEK exhibited elastic orthotropy, with the highest stiffness in the specimen direction corresponding to viscous flow during compression molding. The measured stiffness coefficients indicated a smaller degree of elastic orthotropy in un-reinforced PEEK (Fig. 2), suggesting some macromolecular orientation of the polymer during compression molding (Fig. 2). The increased anisotropy in HA whisker reinforced PEEK specimens, compared to un-reinforced PEEK, was indicative of HA whisker alignment during compression molding. A preferred crystallographic orientation of HA whiskers in HDPE was previously verified by x-ray diffraction [7], and future work will measure the preferred orientation of HA whiskers in PEEK using texture analysis. PEEK reinforced with 40 vol% HA whiskers exhibited an anisotropy ratio (C_{33}/C_{11}) of 1.36, which was comparable to the range 1.37-1.63 reported for the anisotropy ratio between the longitudinal and transverse directions in human cortical bone tissue [4,11,12].

HA whisker reinforced PEEK behaved primarily linear elastic, with little plastic deformation during tensile testing (Fig. 1). The ultimate tensile strength of PEEK reinforced with 20 vol% HA whiskers was near the range of 80-150 MPa typically reported for human cortical bone in the longitudinal direction [14]. PEEK with 40 vol% HA whisker reinforcement exhibited an ultimate tensile strength similar to that of human cortical bone in the transverse direction. PEEK

with 0 vol% HA whisker reinforcement failed with much less plastic deformation than expected. Note that PEEK is a semi-crystalline polymer with a typical crystallinity of 35% and strain-to-failure of 30-35% [15]. SEM micrographs of tensile specimen fracture surfaces showed evidence of brittle failure in both un-reinforced and HA whisker reinforced PEEK (Fig. 4). Therefore, the tensile behavior and fracture surfaces suggest that the processing technique utilized in this study resulted in PEEK with low crystallinity. Whisker pull-out was observed in reinforced PEEK (Fig. 4c and 4d). PEEK adhered to exposed HA whiskers, suggesting a relatively strong interfacial bond.

Table I. Tensile properties for PEEK reinforced with 0, 20 and 40 vol% HA whiskers showing the mean (\pm standard deviation) for each group. Statistically significant differences ($p < 0.01$) existed between each reinforcement level in annealed composites ($n = 5$) for all properties and in as-molded composites for E only ($n = 10$). Differences between as-molded and annealed groups at a given reinforcement level were not statistically significant ($p > 0.09$) for all properties except the ϵ_f at 0 vol% HA whiskers ($p < 0.01$).

HA Content (vol %)	Group	E (GPa)	UTS (MPa)	ϵ_f (%)	w_f (N-mm)
0	as-molded	4.7 (0.2)	83.0 (30.6)	2.0 (0.8)	53.5 (32.8)
20	as-molded	9.5 (0.4)	78.7 (17.4)	0.9 (0.2)	23.1 (10.1)
40	as-molded	17.0 (1.3)	62.5 (25.7)	0.4 (0.2)	8.6 (8.1)
0	annealed	4.6 (0.3)	99.2 (4.6)	2.6 (0.3)	73.8 (12.6)
20	annealed	10.3 (1.6)	75.0 (5.4)	0.8 (0.2)	19.1 (4.5)
40	annealed	17.2 (0.7)	56.3 (8.0)	0.4 (0.1)	6.2 (2.0)

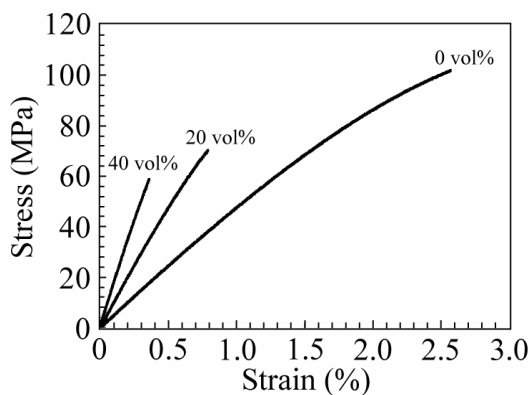


Figure 1. Stress-strain curves for tensile tests of annealed, HA whisker reinforced PEEK composites, showing the median specimen in each group (based on UTS).

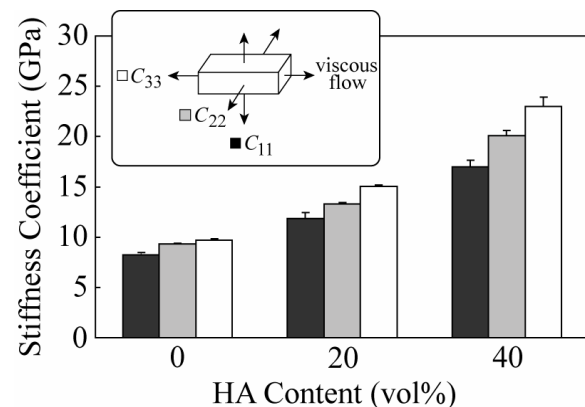


Figure 2. Stiffness coefficients of PEEK reinforced with 0, 20 and 40 vol% HA whiskers showing the mean stiffness in each of the three orthogonal specimen directions. Error bars span the first standard deviation. Statistically significant differences ($p < 0.01$) existed between all groups ($n = 5$).

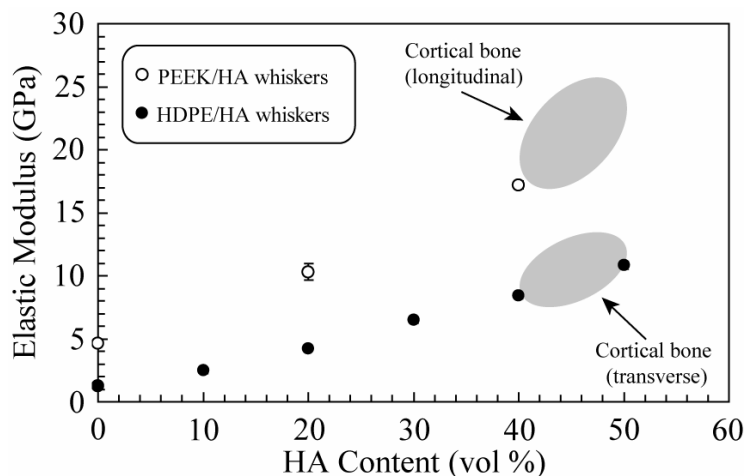


Figure 3. Elastic modulus of annealed, HA whisker reinforced polymer composites in the longitudinal specimen direction versus the reinforcement volume fraction. Error bars span the first standard deviation. Error bars not shown lie within the data point. The upper and lower shaded areas show approximate regions for the elastic moduli of human cortical bone in the longitudinal and transverse directions, respectively. Data for HA whisker reinforced HDPE were adapted from a previous study [7].

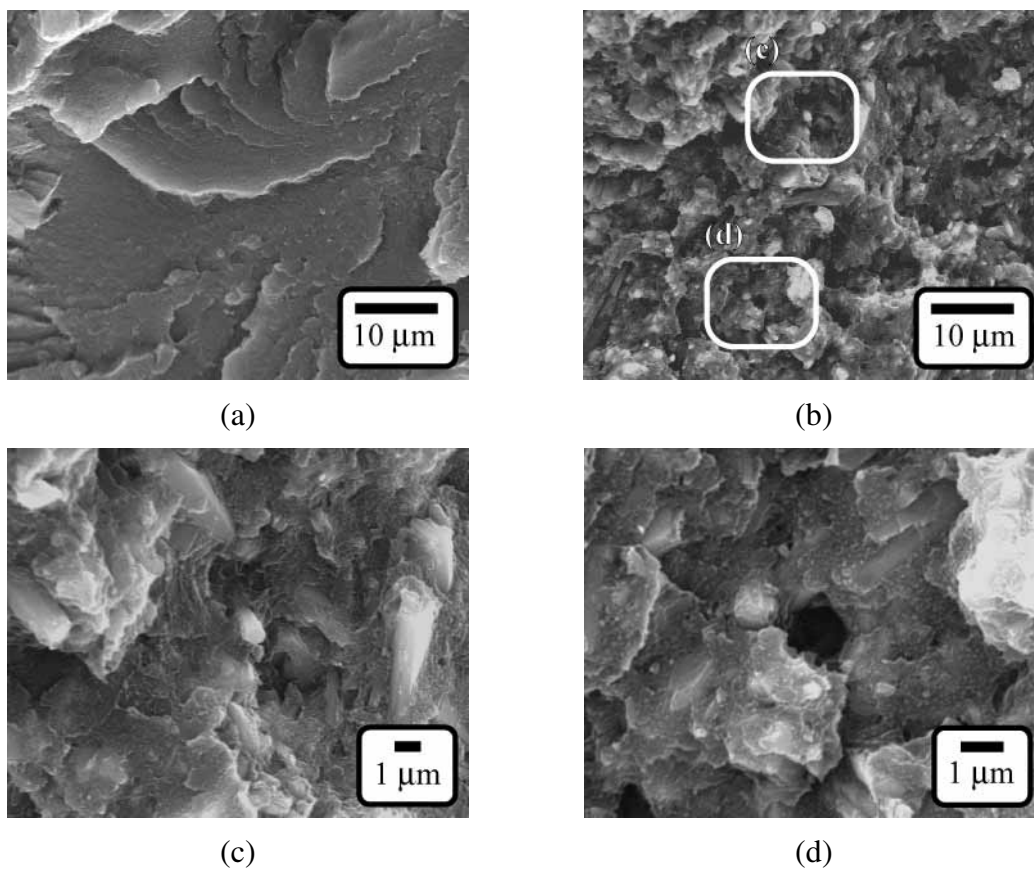


Figure 4. SEM micrographs of fracture surfaces for PEEK reinforced with (a) 0 and (b) 40 vol% HA whiskers, showing brittle failure and (c,d) whisker pullout.

CONCLUSIONS

PEEK was reinforced with up to 40 vol% HA whisker reinforcement using a novel powder processing and compression molding technique. As expected, increased HA whisker reinforcement resulted in increased elastic modulus, but decreased ultimate tensile strength and strain- or work-to-failure. Composites with 40 vol% HA whisker reinforcement possessed elastic constants and elastic anisotropy similar to human cortical bone. Composites with 20 and 40 vol% HA whisker reinforcement exhibited tensile strengths near the ranges typically reported for human cortical bone in the longitudinal and transverse directions, respectively. HA whisker reinforced PEEK is well suited for orthopaedic implants where tailored, bone-mimetic mechanical properties and bioactivity are desired.

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