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Processing and tensile properties of hydroxyapatite-whisker-reinforced polyetheretherketone

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Abstract

Polyetheretherketone (PEEK) was reinforced with 0–50 vol% hydroxyapatite (HA) whiskers using a novel powder processing and compression molding technique which enabled uniform mixing at high whisker content. Texture analysis showed that viscous flow during compression molding produced a preferred orientation of whiskers along the specimen tensile axis. Consequently, the elastic modulus or ultimate tensile strength of HA-whisker-reinforced PEEK was able to be tailored to mimic human cortical bone. PEEK reinforced with 40 and 50 vol% HA whiskers exhibited elastic moduli of 17 and 23 GPa, respectively. Elastic constants were measured using ultrasonic wave propagation and revealed an orthotropic anisotropy also similar to that measured in human cortical bone. PEEK reinforced with 10 and 20 vol% HA whiskers exhibited an ultimate tensile strength of 90 and 75 MPa, respectively. Tensile specimen fracture surfaces showed evidence of brittle failure in both reinforced and un-reinforced PEEK. Whisker pullout was observed with PEEK adhered to HA whiskers, suggesting a relatively strong interface between the PEEK matrix and HA whisker reinforcements.

Keywords: Composite; Elasticity; Hydroxyapatite; Mechanical properties; Microstructure; Polyetheretherketone

1. 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 *c*-axis preferred orientation in directions of principal stress, such as the longitudinal anatomic axis of long bones [1,3–5]. Therefore, bone tissue exhibits corresponding anisotropic mechanical properties [6,7]. The elastic moduli of human cortical bone in the longitudinal and transverse directions are typically reported in the range of 16–23 and 6–13 GPa, respectively [1,2,8–13].

Conventional biomaterials used in most orthopedic implants today have elastic moduli at least an order of magnitude higher (e.g., cobalt chrome, titanium, dense ceramics, etc.) or lower (e.g., polymers) than that of the ECM of bone tissue. The use of materials stiffer than bone tissue can lead to mechanical mismatch problems (e.g., stress shielding) between the implant and the adjacent bone tissue [14,15], where the integrity of the bone/implant interface may be compromised due to the resorption of bone tissue. On the other hand, most polymers do not alone posses sufficient mechanical properties to bear physiological levels of load [16]. Therefore, synthetic biomaterials that are biocompatible, bioactive and able to be tailored to mimic the mechanical properties of bone tissue may be advantageous for implant fixation, synthetic bone graft substitutes, tissue engineering scaffolds, and other orthopedic applications. To this end, numerous biocompatible polymers, including polyethylene [4,17–22], polymethylmethacrylate [23–26], bisphenol-*a*-glycidyl methacrylate (bis-GMA) [27–29], poly(L-lactide) [30–32] and polyetheretherketone (PEEK) [33–35], among others, have been reinforced with bioactive hydroxyapatite (HA).

The seminal work in bone-mimetic, synthetic biocomposites was the development of HAPEX™, a high-density polyethylene (HDPE) matrix reinforced with HA powder [18–22]. The use of HA powder reinforcement resulted in a seven-fold increase in elastic modulus compared to

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un-reinforced HDPE [21]. Injection and compression molded HAPEX^{TM} has been used clinically in orbital floor reconstruction [21,22] and in otologic and maxillofacial surgery [20]; however, the mechanical properties remained insufficient for use in load-bearing devices. Therefore, hydrostatic extrusion was used to further improve the mechanical properties by inducing molecular orientation in the polymer. An elastic modulus of 10–11 GPa was obtained for hydrostatically extruded HAPEX^{TM} using an extrusion ratio of 8:1 [20].

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 dispersed within the HDPE matrix [4]. HA whisker reinforcement resulted in an improved elastic modulus, ultimate tensile strength and work-to-failure compared to HA powder reinforcement [4]. Furthermore, HA whisker reinforcement also resulted in elastic anisotropy similar to that found in human cortical bone tissue [36]. The elastic modulus of compression molded HA-whisker-reinforced HDPE was similar to that of hydrostatically extruded HAPEX^{TM} [20]. However, the elastic moduli of both these composites in the longitudinal direction were only equivalent to that of human cortical bone in the transverse direction, and tensile strengths were still insufficient for use in load-bearing implants. Therefore, further improvement in the mechanical properties was limited, in part, due to the use of HDPE as the matrix phase.

PEEK is a thermoplastic polymer exhibiting biochemical and biomechanical properties suitable for load-bearing orthopedic implants [37–39]. Injection-molded PEEK reinforced with HA powder was recently reported to exhibit mechanical properties approaching those of human cortical bone tissue in the longitudinal direction [33–35]. An elastic modulus in the range of 4–16 GPa and tensile strength in the range of 49–83 MPa was reported for injection-molded PEEK reinforced with 10–40 vol% HA powder [34,35].

The objective of this study was to investigate the ability of HA-whisker-reinforced PEEK to mimic the mechanical properties and anisotropy of human bone ECM. PEEK was reinforced with 0–50 vol% HA whiskers using a novel powder processing and compression molding technique adapted from our previous work with HA-whisker-reinforced HDPE [4]. Tensile properties and elastic constants were measured and compared to human cortical bone tissue as a benchmark.

2. Materials and methods

2.1. Starting powders

A commercially available PEEK powder with a mean particle size of 26 μm (150XF, Victrex USA Inc., Greenville, SC) was used as-received. HA whiskers were synthesized using the chelate decomposition method as described in detail elsewhere [4,40]. Chemical solutions containing 0.10 M lactic acid (Sigma-Aldrich, Inc., St. Louis, MO), 0.03 M phosphoric acid (Sigma-Aldrich), and 0.05 M calcium hydroxide (Aldrich Chemical Company, Inc., Milwaukee, WI) were heated to 200 °C in 2 h and held for 2 h under static conditions in a Teflon lined pressure vessel (Model 4600, Parr Instrument Company, Moline, IL). The as-synthesized HA whiskers were measured by optical microscopy to have a length of 21.6 (+16.9/−9.5) μm, a width of 2.8 (+0.8/−0.6) μm and an aspect ratio of 7.6 (+5.7/−3.2), where the reported values correspond to the mean (±standard deviation) of a log-normal distribution for a sample of 500 whiskers.

2.2. Composite processing

PEEK composites were produced containing 0–50 vol% HA whisker reinforcements. Appropriate amounts of the PEEK powder and the as-synthesized HA whiskers were co-dispersed in ethanol using a sonic dismembrator (Model 500, Fisher Scientific, Pittsburgh, PA). The HA whiskers were added to 20 mL of ethanol and ultrasonically dispersed for 1 min under constant stirring, followed by the PEEK powder with an additional 5 min of ultrasonication under constant stirring. The suspension was wet-consolidated using vacuum filtration immediately following ultrasonic dispersion. The powder mixture was dried overnight in a forced convection oven at 90 °C and uniaxially pressed at 32 MPa using a hydraulic platen press (Model 3912, Carver Laboratory Equipment Inc., Wabash, IN). The resulting powder compact was placed in the center of an open-channel die and compression molded into a 2.6 × 10 × 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 (Model G30H-15-CPX, Wabash MPI, Wabash, IN) with the platens heated to 200 °C. During molding, the composite mixture was extruded bilaterally toward the open ends of the channel die, and a 3 ton clamping force was applied to the die as the polymer solidified. The platens were cooled with chilled water, and the composite bar was removed after the platens reached 100 °C by disassembling the channel die. The composite bar was removed from the channel die before cooling to room temperature in order to mitigate thermal stresses and cracking.

ASTM D638 type V tensile specimens [41] were machined from the composite bar 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 at 200 °C for 4 h. The oven was cooled to 150 °C in 4 h in order to allow recrystallization of the polymer. The as-molded group consisted of composites containing 0, 20 and 40 vol% HA whiskers with ten tensile specimens prepared for each reinforcement level. The annealed group consisted of composites containing 0, 10, 20, 30, 40 and 50 vol% HA whiskers with five tensile specimens prepared for each reinforcement level.

2.3. Tensile properties

Tensile tests were performed in accordance with ASTM D638 with a crosshead speed of 1.0 mm/min [41]. Specimens were loaded under uniaxial tension using an electromagnetic test instrument (ELF 3300, Bose Corp., ElectroForce Systems Group, Eden Prairie, MN). 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). A digital extensometer (Model 3442, Epsilon Technology Corp., Jackson, WY) was used to monitor displacement within the specimen gage length for an accurate measure of strain. Failure surfaces of tensile specimens were coated with Au-Pd by sputter deposition and examined using a scanning electron microscope (SEM) (Evo 50, LEO Electron Microscopy Ltd., Cambridge, UK) with an accelerating voltage of 20 kV and a working distance of 6 mm.

2.4. Anisotropy

The elastic anisotropy of annealed composites was characterized using an ultrasonic wave propagation technique [12,42]. Annealed composite bars were sectioned into specimens with nominal dimensions of $10 \times 10 \times 2.6$ mm using a low speed diamond wafer saw. Five specimens were prepared for each reinforcement level, which included 0, 20 and 40 vol% HA whiskers. The first three elastic constants from the main diagonal of the reduced fourth-order stiffness tensor, C_{ii}, were calculated as $C_{ii} = \rho v_i^2$ $(i = 1, 2, 3)$, where ρ is the apparent specimen density, v_i is the transmitted wave velocity, and i is an integer corresponding to the three mutually orthogonal specimen axes. The apparent specimen density was measured using Archimedes' principle [11,42,43]. Dilational ultrasonic waves were transmitted to and received from the specimen using 2.25 MHz transducers and a pulser/receiver unit (Models 5800 and V106RM, Panametrics Inc., Waltham, MA). Deionized water was used as a coupling fluid between the specimens and transducers. The transmitted wave velocity in the ith specimen direction was calculated as $v_i = d_i/\Delta t$ where d_i is the specimen dimension in the direction of wave propagation and Δt is the time delay for wave transmission. Specimen dimensions were measured using digital calipers accurate to ± 0.01 mm. The time delay, Δt, for wave transmission through the specimen was measured using an oscilloscope (TDS 2012, Tektronix Inc., Beaverton, OR). The specimen axes were defined by the composite bar length $(i = 3)$, width $(i = 2)$ and thickness $(i = 1)$, such that C_{33} corresponded to the direction of flow along the specimen length during compression molding and C_{11} corresponded to direction of applied force during compression molding.

Quantitative measurement of the preferred orientation of HA whiskers in composites was performed using a General Area Detector Diffraction System (GADDS) equipped with a two-dimensional HI-STAR detector (Bruker AXS Inc., Madison, WI). Selected specimens were sectioned from annealed composite bars within the same regions corresponding to the gage length of tensile specimens using a low speed diamond wafer saw. The surface orthogonal to the longitudinal specimen direction was polished to a 0.05 μm final surface finish using as series of diamond polishing compounds and colloidal Al_2O_3. Polished specimens were mounted on the goniometer and aligned using a laser-video microscope. Monochromatic Cu Kα radiation was generated at 40 kV and 40 mA and focused on the specimen by a 0.5 mm diameter pinhole collimator. The distance between the specimen surface and detector was set to 60 mm.

Two-dimensional diffraction patterns were collected for HA-whisker-reinforced PEEK composites at each reinforcement volume fraction. The 002, 222 and 213 reflections for HA were chosen due to relatively sharp distinction and their relationship to the crystal habit of HA whiskers. Selected composite specimens were rotated about the longitudinal specimen axis in 5° increments and a total of 72 diffraction patterns were obtained over the orientation space. The diffraction patterns were integrated using the GADDS software to determine the 002, 222 and 213 pole figures. This method made no assumptions regarding the symmetry of the HA whisker orientation distribution. However, the results revealed an axisymmetric HA whisker orientation distribution. Therefore, data collection was improved by assuming an axisymmetric HA whisker orientation distribution. Composite specimens were continuously rotated about the longitudinal specimen axis and the diffraction patterns were integrated using the GADDs software to determine the 002, 222 and 213 pole figures. Pole figure data was corrected by eliminating background intensity differences using an untextured reference pole figure for HA-powder-reinforced polymer composites. The three corrected pole figures for the 002, 222 and 213 reflections were combined and the orientation distribution function (ODF) was calculated using the arbitrarily defined cells (ADC) method (LaboTex, Version 2.1, LaboSoft s.c., Krakow, Poland). Finally, inverse pole figures and pole figures were calculated from ODFs and plotted to represent the texture. The degree of preferred orientation was quantified in multiples of a random distribution (MRD), where MRD = 1 corresponds to a random distribution.

2.5. Statistical methods

One-way analysis of variance (ANOVA) (JMP 5.1, SAS Institute Inc., Cary, NC) was used to compare mechanical properties between experimental groups. Post hoc comparisons were performed using an unpaired Student's T-test with a level of significance of 0.05. Two-way ANOVA was used to examine the effects and interaction of the reinforcement level and annealing treatment (vs. as-molded) on the measured tensile properties, as well as the effects and interaction of the reinforcement level and specimen direction on the measured elastic constants.

3. Results

3.1. Composite processing

HA-whisker-reinforced PEEK composites were reliably produced with 0–50 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 temperatures below 345 °C generally cracked or solidified before reaching the desired thickness. Areas of un-melted 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, in particular the ultimate tensile strength and work-to-failure, of as-molded composites exhibited substantial inter-specimen variability, which was alleviated by employing the annealing treatment described above (Table 1).

3.2. Tensile properties

Tensile tests showed that increased HA whisker reinforcement resulted in increased elastic modulus, as expected (Table 1, Figs. 1 and 2a). As-molded and annealed PEEK composites reinforced with 40 vol% HA whiskers exhibited elastic moduli on the order of 17 GPa (Table 1, Fig. 2a). Two-way ANOVA showed a statistically significant effect of the reinforcement level on the elastic modulus ($p < 0.001$, Table 2). Neither the effect of annealing nor the interaction with the reinforcement level were significant (Table 2). Differences in the elastic modulus between all reinforcement levels for both as-molded and annealed composites were statistically significant ($p < 0.01$), but differences between the annealed and as-molded composites for a given reinforcement level were not statistically significant ($p > 0.09$, Table 1).

The ultimate tensile strength of as-molded and annealed composites decreased with increased HA whisker reinforcement (Table 1, Figs. 1 and 2b). As-molded and annealed PEEK composites reinforced with up to 20 vol% HA whiskers exhibited a mean ultimate tensile strength of at least 75 MPa (Table 1, Fig. 2b). Two-way ANOVA showed a statistically significant effect of the reinforcement level on the ultimate tensile strength ($p < 0.001$, Table 2). Neither the effect of annealing nor the interaction with reinforcement level were significant (Table 2). Differences

Table 1
Tensile properties for as-molded and annealed PEEK reinforced with 0–50 vol% HA whiskers showing the mean (±standard deviation) elastic modulus (E), ultimate tensile strength (UTS), strain-to-failure (ε_f) and work-to-failure (w_f) for each group

HA content (vol%)	Processing method	E (GPa)	UTS (MPa)	ε_f (%)	w_f (N-mm)
0	As-molded	4.7 (0.2)	83.5 (28.9)	2.0 (0.7)	53.5 (32.8)
0	Annealed	4.6 (0.3)	99.2 (4.6)	2.6 (0.3)	73.8 (12.6)
10	Annealed	7.3 (0.5)	90.0 (6.2)	1.6 (0.1)	46.6 (7.9)
20	As-molded	9.5 (0.4)	78.7 (17.4)	0.9 (0.2)	23.1 (10.1)
20	Annealed	10.3 (1.6)	75.0 (5.4)	0.8 (0.2)	19.1 (4.5)
30	Annealed	13.0 (0.3)	66.7 (6.9)	0.5 (0.1)	10.9 (2.9)
40	As-molded	17.0 (1.3)	62.5 (25.7)	0.4 (0.2)	8.6 (8.1)
40	Annealed	17.2 (0.7)	56.3 (8.0)	0.4 (0.1)	6.2 (2.0)
50	Annealed	23.2 (0.6)	41.9 (22.6)	0.2 (0.1)	2.8 (2.7)

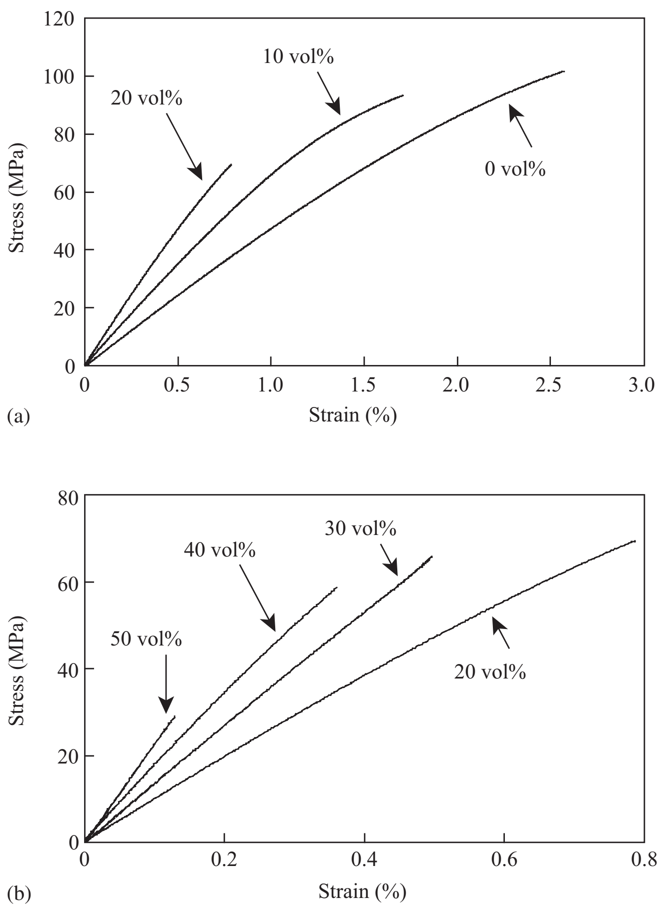

Fig. 1. Representative stress-strain curves for tensile tests of annealed PEEK composites reinforced with (a) 0, 10 and 20 vol% and (b) 20, 30, 40 and 50 vol% HA whiskers. The median specimen for each group is shown based the on the ultimate tensile strength.

in ultimate tensile strength between as-molded and annealed composites for a given reinforcement level were not statistically significant ($p>0.6$), although the variability exhibited by as-molded composites was much higher than for annealed composites (Table 1).

The strain- and work-to-failure of as-molded and annealed composites decreased with increased HA whisker reinforcement, as expected (Table 1, Figs. 1 and 2c). Two-way ANOVA showed a statistically significant effect of the reinforcement level on the strain- and work-to-failure ($p<0.001$, Table 2). The effect of annealing was not significant for both the strain- and work-to-failure; however, there was a statistically significant interaction with the reinforcement level for the strain-to-failure ($p<0.05$, Table 2). Differences in the strain- or work-to-failure between the annealed and as-molded groups for a given reinforcement level were not statistically significant ($p>0.6$) except for a difference in un-reinforced PEEK ($p<0.05$, Table 1). Un-reinforced PEEK exhibited primarily linearly elastic deformation (Fig. 1), with strain- and work-to-failure in the range of 2.0–2.6% and 53–74 N mm, respectively (Fig. 2c). Non-linear deformation decreased with increased HA whisker reinforcement. PEEK reinforced with 30–50 vol% HA whiskers exhibited virtually no plastic deformation (Fig. 1). SEM micrographs of tensile specimen fracture surfaces showed evidence of brittle failure in both un-reinforced and HA-whisker-reinforced PEEK (Fig. 3). However, whisker pull-out was observed in reinforced PEEK with PEEK adhered to exposed HA whiskers (Figs. 3c and d).

3.3. Anisotropy

The elastic constants and elastic anisotropy of annealed composites increased with increased HA whisker reinforcement (Fig. 4). Two-way ANOVA showed a statistically significant effect of the reinforcement level and specimen direction (C_{11}, C_{22} or C_{33}) on the stiffness, as well as an interaction between the two factors ($p<0.001$). Differences between all stiffness coefficients (C_{11}, C_{22} and C_{33}) at a given reinforcement level and between reinforcement levels for a given stiffness coefficient were statistically significant ($p<0.01$). Thus, HA-whisker-reinforced PEEK exhibited elastic orthotropy, with the highest stiffness in the specimen direction corresponding to viscous flow during molding (C_{33}) and the lowest stiffness in the direction of compression during molding (C_{11}) (Fig. 4). PEEK reinforced with 0, 20 and 40 vol% HA whiskers exhibited mean (± standard deviation) elastic anisotropy ratios

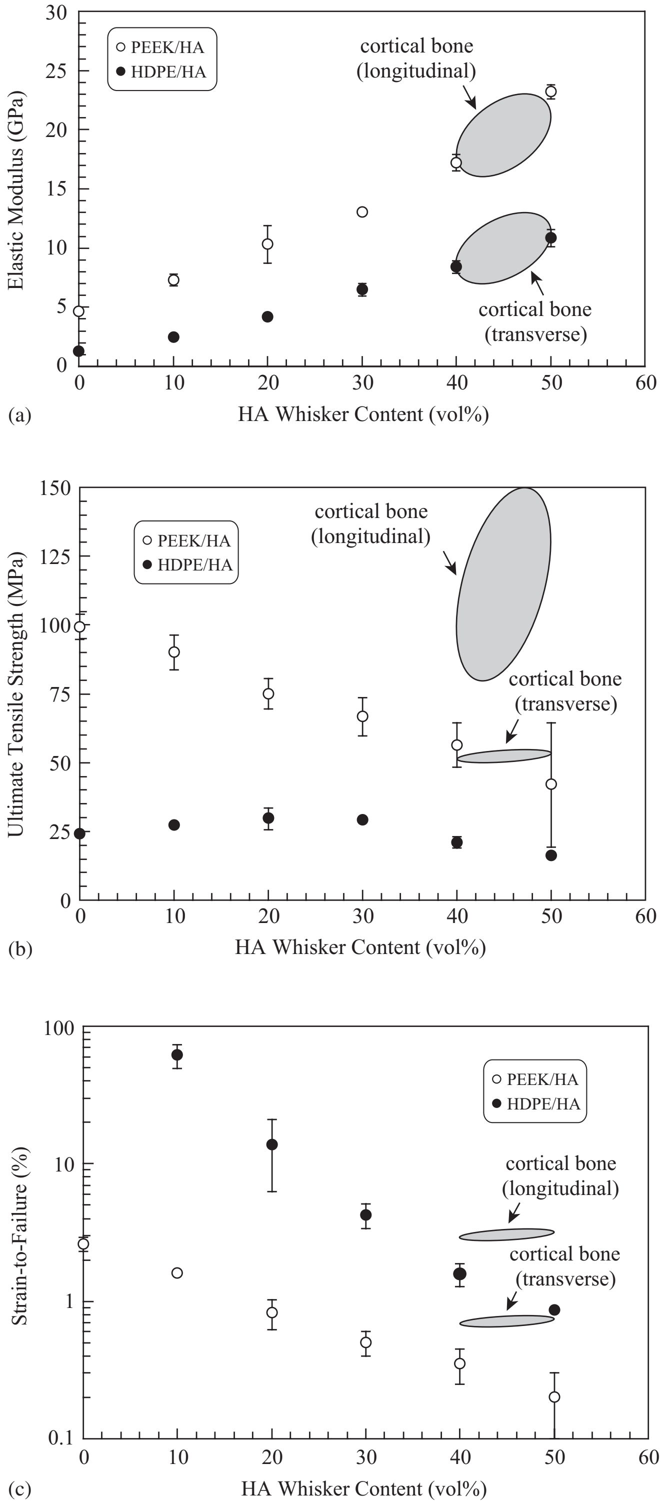

Fig. 2. (a) Elastic modulus, (b) ultimate tensile strength and (c) strain-to-failure of HA-whisker-reinforced polymer composites in the longitudinal specimen direction versus the reinforcement volume fraction. Error bars span the first standard deviation. Error bars not shown lie within the data point. The upper and lower shaded areas on each plot show approximate regions for the given mechanical property in the longitudinal and transverse directions, respectively, of human cortical bone tissue. Data for HA-whisker-reinforced HDPE were adapted from a previous study for comparison [4]. The effect of the HA whisker content on each tensile property was statistically significant ($p<0.0001$) for both PEEK and HDPE composites.

Table 2
Results of two-way ANOVA for the effects of the HA whisker content and processing method (as-molded vs. annealed) on the measured elastic modulus (E), ultimate tensile strength (UTS), strain-to-failure (ε_f) and work-to-failure (w_f)

Measurement	HA Content (vol%)	Processing method	HA content × processing
E (GPa)	$p<0.0001$	$p=0.27$	$p=0.44$
UTS (MPa)	$p<0.001$	$p=0.73$	$p=0.30$
ε_f (%)	$p<0.0001$	$p=0.23$	$p<0.05$
w_f (N-mm)	$p<0.0001$	$p=0.36$	$p=0.11$

(C_{33}/C_{11}) of 1.18 (0.05), 1.27 (0.06) and 1.36 (0.11), respectively (Fig. 4). Thus, the degree of elastic anisotropy increased with increased HA content ($p<0.01$). The elastic anisotropy ratio in the plane normal to the longitudinal specimen axis (C_{22}/C_{11}) was not affected by increased HA content ($p=0.18$).

Quantitative texture analysis indicated a c-axis preferred orientation of HA whiskers in the longitudinal specimen axis (Fig. 5), which coincided with the tensile axis or C_{33} in mechanical tests and the direction of viscous flow during compression molding (Fig. 4). The maximum degree of HA whisker c-axis preferred orientation in the longitudinal specimen axis was 2.50 and 2.56 MRD for PEEK reinforced with 20 and 40 vol% HA whiskers, respectively Fig. 5). In the plane normal to the longitudinal specimen axis, differences in the HA whisker c-axis preferred orientation were insignificant. Therefore, HA-whisker-reinforced PEEK exhibited an axisymmetric orientation distribution, or a fiber texture.

4. Discussion

4.1. Bone-mimetic mechanical properties

Healthy human bone tissue exhibits substantial variation in mechanical properties depending on the tissue density and microstructure. In conventional mechanical tests (e.g., tensile or compression tests), cancellous bone exhibits significantly lower effective mechanical properties compared to cortical bone, due to a significantly higher porosity. The relative porosity of cortical and cancellous bone are typically on the order of 5–10% and 75–95%, respectively [9]. Therefore, the mechanical properties of cortical bone provide a reasonable approximation for the "material" properties of the mineralized ECM of human bone tissue and were used as the benchmark for this study.

Results from tensile tests indicated that the longitudinal elastic modulus of HA-whisker-reinforced PEEK was tailored to mimic human cortical bone (Fig. 2a). The elastic modulus of human cortical bone in the longitudinal direction is typically reported in range of 16–23 GPa [1,2,8–13]. PEEK reinforced with 40 and 50 vol% HA

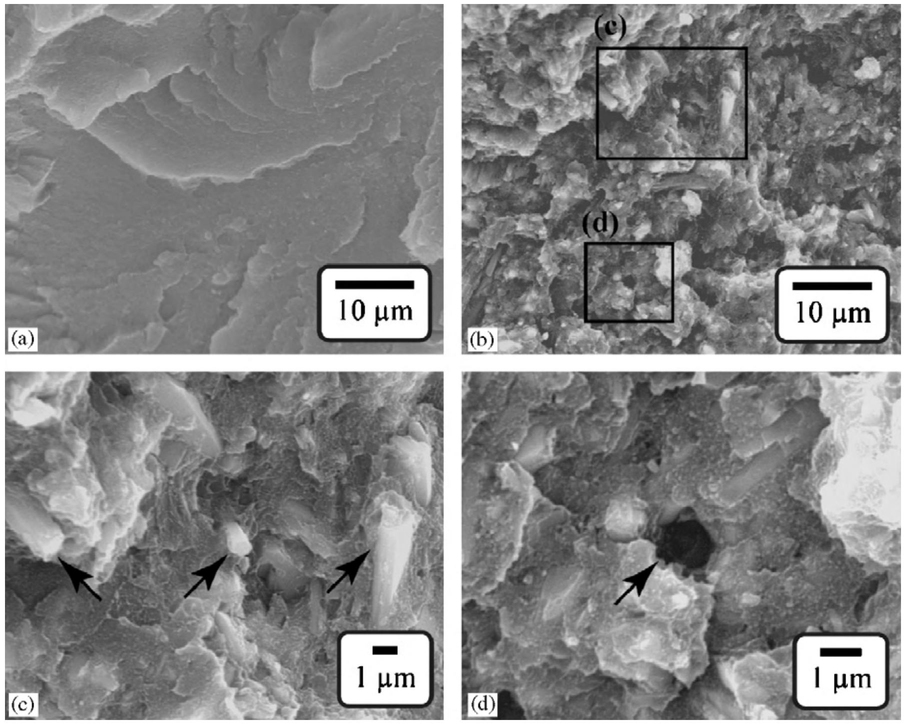

Fig. 3. SEM micrographs of fracture surfaces for PEEK reinforced with (a) 0 and (b) 40 vol% HA whiskers, showing brittle failure and (c, d) whisker pullout. Whiskers and cavities on the fracture surface are shown by arrows in (c) and (d), respectively.

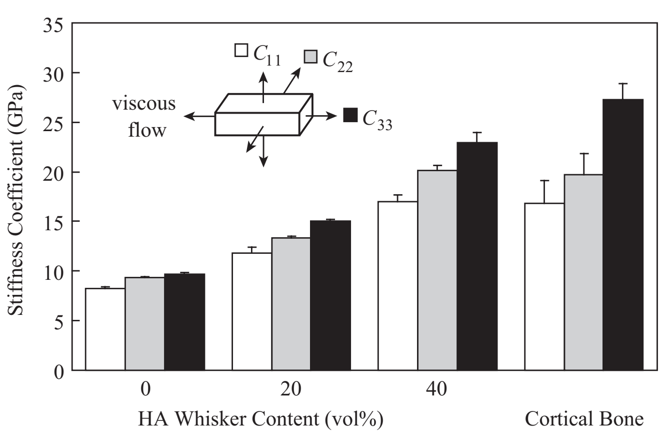

Fig. 4. Elastic constants for PEEK reinforced with 0, 20 and 40 vol% HA whiskers, compared to measurements taken on human cortical bone [42], showing the mean stiffness coefficient in each of three orthogonal specimen directions. Stiffness coefficients for human cortical bone were measured in the radial, circumferential and longitudinal anatomic directions of a human femur (shown left to right). Error bars span the first standard deviation. Statistically significant differences ($p<0.01$) existed between all groups and coefficients for PEEK composites. A statistically significant difference ($p<0.001$) existed between PEEK reinforced with 40 vol% HA whiskers and human cortical bone for C_{33}, but C_{22} and C_{11} other were not significantly different ($p>0.05$).

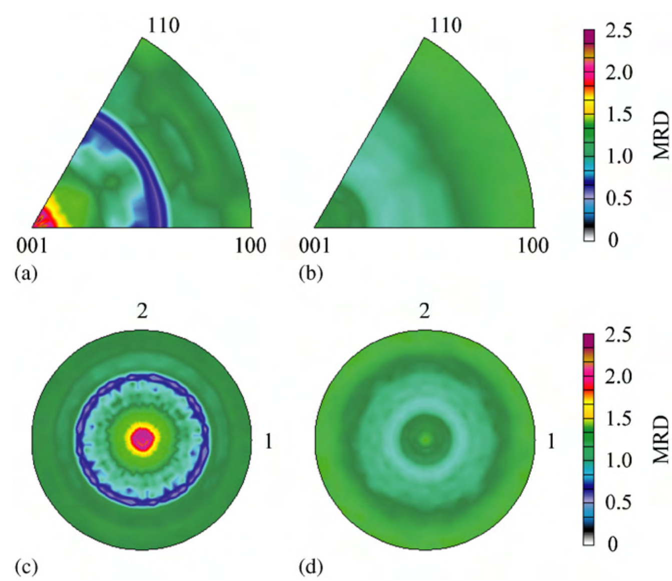

Fig. 5. Inverse pole figures calculated from the ODF for PEEK reinforced with 40 vol% HA whiskers, showing the (a) longitudinal (3) and (b) transverse (1 or 2) specimen axes plotted in the crystallographic space shown. Pole figures recalculated from the ODF for the same specimen in (a, b), showing the (c) 001 and (d) 100 crystallographic axes plotted on a stereographic projection of the specimen orientation space defined by the longitudinal (3, coming out of the paper) and transverse (1 and 2, in the plane of the paper) specimen axes. The orientation distribution is shown in units of multiples of a random distribution (MRD).

whiskers exhibited elastic moduli in the range of 17–23 GPa (Table 1). Also, note that HA-whisker-reinforced PEEK resulted in a higher elastic modulus at a given reinforcement level compared to HA-powder-reinforced PEEK composites from previous studies, as expected [34,35].

The ultimate tensile strength of HA-whisker-reinforced PEEK was similar to that of human cortical bone in the longitudinal direction (Fig. 2b), which is typically reported in the range of 80–150 MPa [9,10,13]. PEEK reinforced with 10 and 20 vol% HA whiskers exhibited ultimate tensile strengths in the range of 75–90 MPa (Table 1). At higher reinforcement levels, however, the ultimate tensile strength was only similar to that of human cortical bone in the transverse direction (Fig. 2b). Thus, a bone mimetic elastic modulus and ultimate tensile strength were not obtained at the same level of reinforcement. Note that the composites in this study mimic the ultrastructure of bone ECM, whereas cortical bone tissue also contains hierarchical structural features, such as lamellae and osteons, which also act as reinforcements.

The strain-to-failure of HA-whisker-reinforced PEEK was lower than that of human cortical bone (Fig. 2c), which has been reported to be on the order of 3% [13]. Unreinforced PEEK exhibited a similar strain-to-failure as cortical bone, but failed at lower strains and with less plastic deformation than expected. PEEK is a semi-crystalline polymer with a typical crystallinity of 30–35% and strain-to-failure of 30–35% [39]. Therefore, the tensile properties and fracture surfaces suggest that the relatively slow cooling rate used in this study for both the as-molded and annealed composites resulted in PEEK with relatively high crystallinity and low ductility [44]. Furthermore, PEEK crystallites have been shown to nucleate preferentially at the interface with reinforcements resulting in increased interfacial strength [44]. As mentioned above, PEEK was adhered to HA whiskers exposed on tensile specimen fracture surfaces (Fig. 3). This suggests a relatively strong interface between the PEEK matrix and HA whisker reinforcements which might have limited energy dissipation by crack bridging or deflection.

The elastic constants measured for PEEK reinforced with 40 vol% HA whiskers were comparable to those measured for cortical bone from a human femur (Fig. 4). Mean stiffness coefficients for human cortical bone in the longitudinal (C_{33}), circumferential (C_{22}) and radial (C_{11}) directions were measured to be 27.3, 19.8 and 16.8 GPa [42], compared to 23.0, 20.1 and 17.0 GPa for PEEK reinforced with 40 vol% HA whiskers, respectively. Differences between human cortical bone and PEEK reinforced with 40 vol% HA whiskers were not statistically significant ($p>0.66$), except for a statistically significant difference in C_{33} ($p<0.001$).

The elastic orthotropy exhibited by HA-whisker-reinforced PEEK was qualitatively similar to human cortical bone [11,12,42]. However, the mean ($\pm$standard deviation) degree of elastic anisotropy (C_{33}/C_{11}) for PEEK reinforced with 40 vol% HA whiskers was 1.36 (0.11) compared to 1.67 (0.26) for human cortical bone tissue [42] ($p<0.01$). The elastic anisotropy ratio in the plane normal to the longitudinal specimen axis (C_{22}/C_{11}) was not statistically different from human cortical bone tissue ($p>0.4$). Therefore, the difference in C_{33}/C_{11} was due to the greater magnitude of C_{33} in cortical bone (Fig. 4). The greater magnitude of C_{33} in human cortical bone might seem to be due to the additional reinforcement by lamellae and osteons at higher levels of structural organization that are not present in HA-whisker-reinforced PEEK. However, in cortical bone, nanoindentation measurements for the elastic modulus of the ECM were generally similar to measurements by conventional mechanical tests at the tissue level [8], which suggests that the reinforcing effect of osteons at the tissue level is mitigated by the presence of intra-cortical porosity. Therefore, differences in the apatite crystal volume fraction, aspect ratio and *c*-axis preferred orientation were more likely the cause of the greater magnitude of C_{33} in human cortical bone compared to PEEK reinforced with 40 vol% HA whiskers.

4.2. Bone-mimetic microstructure

HA-whisker-reinforced PEEK composites were able to be processed at high reinforcement levels. Interestingly, composites exhibiting an elastic modulus similar to that of human cortical bone were processed with a HA whisker content (40–50 vol%), which was also similar to the level of apatite reinforcement in human bone tissue [1,2]. The HA content is not only important for biomechanical behavior but also biochemical behavior. HDPE reinforced with HA powder exhibited increased osteoblast activity with increased HA content, on the order of that present in bone tissue [19].

Texture analysis revealed a preferred crystallographic and morphological orientation of the HA whisker reinforcements in PEEK (Fig. 5). The maximum degree of HA whisker *c*-axis preferred orientation in the longitudinal specimen axis was on the order of 2.5 MRD for PEEK reinforced with 20 or 40 vol% HA whiskers (Fig. 5). Recall that MRD = 1 corresponds to a random orientation distribution. The degree of the preferred orientation in HA-whisker-reinforced PEEK was similar to that of apatite crystals in human cortical bone tissue. The maximum degree of apatite crystal *c*-axis preferred orientation in the longitudinal anatomic axis was also on the order of 2.5 MRD for tissue from the mid-diaphysis of a human femur [5]. The preferred orientation of apatite in bone is thought to be determined by guided nucleation and growth of crystals within collagen fibrils, and a hypothesized mechanosensory mechanism for crystals residing outside collagen fibrils [6]. The preferred orientation of HA whisker reinforcements in PEEK was a result of the novel processing technique used in this study. During compression molding, the viscous composite mixture of PEEK and HA whiskers was bi-laterally extruded from the center toward the open ends of the channel die. Thus, shear forces acted to align the HA whisker reinforcements in the direction of viscous flow.

The alignment of HA whiskers within the PEEK matrix contributed to the elastic orthotropy of the composites. The highest stiffness was measured in the direction parallel to the preferred orientation of HA whiskers (Figs. 4 and 5). The measurement of stiffness coefficients also revealed a degree of anisotropy similar to that of human cortical bone. Although the mean anisotropy ratio measured for PEEK reinforced with 40 vol% HA whiskers ($C_{33}/C_{11} = 1.36$) was statistically different from that measured for the human cortical bone specimens cited ($C_{33}/C_{11} = 1.67$), it was within the range of means ($C_{33}/C_{11} = 1.3$–1.8) reported in the literature for a broader sampling of cortical bone specimens [6,7,11,12,42].

4.3. Composite design and processing

The use of PEEK as the matrix phase resulted in dramatically improved elastic modulus and ultimate tensile strength, but decreased work-to-failure compared to HA-whisker-reinforced HDPE (Fig. 2). HA-whisker-reinforced HDPE achieved an elastic modulus similar to the transverse direction of human cortical bone [4], while HA-whisker-reinforced PEEK exhibited an elastic modulus similar that of human cortical bone in the longitudinal direction at similar reinforcement levels (Fig. 2a). Similarly, the ultimate tensile strength was dramatically improved, up to three-fold, using PEEK compared to HDPE at similar reinforcement levels (Fig. 2b). The inferior mechanical properties of the HDPE matrix limited the application of these composites to non-load-bearing devices [20–22]. The similarities between the elastic modulus and ultimate tensile strength for HA-whisker-reinforced PEEK and those of human cortical bone make HA-whisker-reinforced PEEK a possible candidate for orthopedic implants which must bear physiological levels of load.

HA-whisker-reinforced PEEK composites were processed reliably over a wide range of HA-whisker-reinforcement levels (0–50 vol%) using a novel powder processing and compression molding technique, resulting in composites with tailored mechanical properties. Compounding and other melt mixing processes have been used to reinforce PEEK with up to 40 vol% HA powder [33–35], but higher levels were limited by the high viscosity of the polymer melt. The powder mixing approach used in this study circumvented this limitation enabling uniform mixing for up to 50 vol% reinforcement. Nonetheless, the process was not without room for further improvement in the mechanical properties of the composites.

A small degree of warping, presumably due to non-uniform heat transfer during solidification of the polymer melt, and/or gradation in the HA content or orientation through the specimen thickness, was observed in some of the tensile specimens, especially those with high HA content. Warping may have resulted in an artificially low ultimate tensile strength and strain-to-failure due to the bending moment imparted on warped tensile specimens by the clamps prior to testing. For example, PEEK reinforced with 50 vol% HA whiskers exhibited the greatest variability in mechanical properties; however, two tensile specimens exhibited a significantly higher ultimate tensile strength (>65.0 MPa) and strain-to-failure ($\approx 0.3\%$) compared to other specimens in the group (Table 1). These specimens also exhibited a noticeably lower degree of warping compared to the other specimens in this group. Interestingly, these two specimens were machined from the same composite bar, which suggests that further optimization of the process will result in higher quality composites with ultimate tensile strength exceeding 65 MPa even at 50 vol% HA whiskers.

The strain or work-to-failure of the composites processed in this study fell short of that for human cortical bone tissue. Improvements in strain-to-failure are expected to be realized by more precise control of the cooling rate after molding. An increased cooling rate is known to decrease the PEEK crystallinity and increase the ductility of composites [44], which warrants further study.

5. Conclusions

PEEK was reinforced with up to 50 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, strain-to-failure and work-to-failure. Composites with 40–50 vol% HA whisker reinforcement exhibited elastic moduli similar to that of human cortical bone in the longitudinal direction. Composites with 10 and 20 vol% HA whisker reinforcement exhibited tensile strengths similar to that of human cortical bone in the longitudinal direction. The compression molding technique resulted in a preferred orientation of HA whisker reinforcements in the direction of viscous flow. Additionally, a degree of elastic anisotropy similar to that of human cortical bone was observed in PEEK with 40 vol% HA whisker reinforcement. Thus, HA-whisker-reinforced PEEK is well suited for orthopedic implants where tailored, bone-mimetic mechanical properties and bioactivity are desired.

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