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Research paper

Mechanical properties of hydroxyapatite whisker reinforced polyetherketoneketone composite scaffolds

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ABSTRACT

The apparent mechanical properties of hydroxyapatite (HA) whisker reinforced polyetherketoneketone (PEKK) scaffolds were evaluated in unconfined, uniaxial compression to investigate the effects of the porosity (75%, 82.5% and 90%), HA content (0, 20 and 40 vol%) and mold temperature (350, 365 and 375 °C). Increased porosity resulted in a non-linear decrease in the elastic modulus and yield strength for both reinforced and unreinforced PEKK scaffolds, as expected. The increase in elastic modulus and yield strength with increased relative density followed a power-law, similar to trabecular bone and other open-cell foams. HA whisker reinforcement generally resulted in an increased elastic modulus from 0 to 20 vol% HA and a subsequent decrease from 20 to 40 vol% HA, while the yield strength and strain were decreased in scaffolds with 40 vol% HA compared to those with 0 or 20 vol% HA. Increased mold temperature resulted in an increased elastic modulus, yield strength and yield strain. These effects enabled the mechanical properties to be tailored to mimic human trabecular bone. The elastic modulus was greater than 50 MPa, and the yield strength was greater than 0.5 MPa, for scaffolds with 75% porosity at all combinations of reinforcement level and mold temperature. Scaffolds with 75% porosity and 20 vol% HA molded at 375 °C exhibited a mean elastic modulus and yield strength of 149 MPa and 2.2 MPa, respectively, which was the highest of the conditions investigated in this study and similar to human vertebral trabecular bone. Therefore, HA whisker reinforced PEKK scaffolds may be advantageous for permanent implant fixation, including interbody spinal fusion.

1. Introduction

A number of porous scaffold materials have been prepared and investigated for use in orthopaedic applications, including bone ingrowth scaffolds for permanent implant fixation, as well as tissue engineering scaffolds and synthetic bone graft substitutes for tissue regeneration. Commercialized bone ingrowth scaffolds for permanent implant fixation include sintered beads, wire meshes and foams composed of titanium alloys, cobalt-chrome alloys and tantalum (Ryan et al., 2006). These metallic scaffolds are generally biocompatible and osteoconductive, but are not bioactive which may limit long-term osteointegration. Furthermore, the high x-ray attenuation of metals inhibits post-operative radiographic analysis of bone ingrowth, which is particularly important for interbody spinal fusion (Kurtz and Devine, 2007; Toth et al., 2006). Finally, the greater stiffness of metals limits load transfer to the peri-implant tissue, which is typically trabecular

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bone, shielding bone cells and tissue from the mechanical stimulus necessary for new bone formation.

Scaffold materials for tissue regeneration typically comprise biodegradable polymers that are intended to be gradually replaced by new tissue concurrent with degradation (Agrawal and Ray, 2001; Rezwan et al., 2006). Calcium phosphate fillers, such as hydroxyapatite (HA), are often added in order to provide bioactivity, improve mechanical properties, and buffer acidic degradation products (Jung et al., 2005; Kim et al., 2006; Kothapalli et al., 2005; Mathieu et al., 2006; Rezwan et al., 2006; Teng et al., 2006; Thomson et al., 1998; Weng et al., 2002; Zhang and Ma, 1999). While one noteworthy study reported an apparent compressive modulus and strength of approximately 175 and 3.5 MPa, respectively (Mathieu et al., 2006), most degradable polymer and composite scaffolds with at least 75% porosity have exhibited an apparent compressive modulus and yield strength less than 50 and 0.5 MPa, respectively, which is lower than human trabecular bone and unlikely to be sufficient for bearing physiological loads. This may be acceptable for tissue engineering scaffolds and synthetic bone graft substitutes provided that tissue regeneration rapidly restores mechanical function as the degradable scaffold is replaced. However, permanent implant fixation requires that the scaffold possess immediate and long-term mechanical integrity.

A non-degradable polymer scaffold for implant fixation could enable radiographic analysis of bone ingrowth and improve osteointegration by exhibiting mechanical properties similar to the peri-implant tissue. Polyaryletherketones (PAEKs) are semi-crystalline thermoplastic polymers exhibiting biocompatibility, as well as biochemical and biomechanical properties suitable for load-bearing orthopaedic implants (Evans and Gregson, 1998; Kurtz and Devine, 2007; Toth et al., 2006). Dense HA reinforced PAEK composites have been reported to exhibit mechanical properties similar to those of human cortical bone tissue (Abu Bakar et al., 2003a,b; Converse et al., 2007; Tang et al., 2004). HA whiskers were demonstrated to result in improved tensile and fatigue properties, compared to conventional HA powders, at a given reinforcement level in polymers (Kane et al., 2008; Roeder et al., 2003, 2008). Compression molded polyetheretherketone (PEEK) reinforced with 0–50 vol% HA whiskers exhibited an elastic modulus in the range 4–23 GPa and tensile strength in the range 42–99 MPa (Converse et al., 2007).

Porous HA reinforced PAEK scaffolds have been prepared by two methods. HA powder reinforced PEEK scaffolds were processed using selective laser sintering (SLS) (Tan et al., 2003, 2005a,b); however, the attainable level of porosity depended on both the reinforcement level and the laser power and was limited to 70%–74% (Tan et al., 2005b). Additionally, scaffolds became fragile as the HA content was increased, which limited the HA content to 40 wt%, or ∼22 vol% (Tan et al., 2003, 2005a). More recently, HA whisker reinforced polyetherketoneketone (PEKK) scaffolds were prepared using a combination of powder processing, compression molding and particle leaching methods (Converse and Roeder, in press). Scaffolds with 75%–90% porosity and 0–40 vol% HA whisker reinforcement exhibited architectural and microstructural characteristics known to be favorable for osteointegration (Fig. 1). Scaffold porosity was interconnected with a mean pore size in the range 200–300 μm as measured by micro-computed tomography (micro-CT) (Fig. 1(a)). HA whiskers were embedded within and exposed on the surface of scaffold struts, producing a micro-scale surface topography, shown by von Kossa staining and scanning electron microscopy (SEM) (Fig. 1(c)).

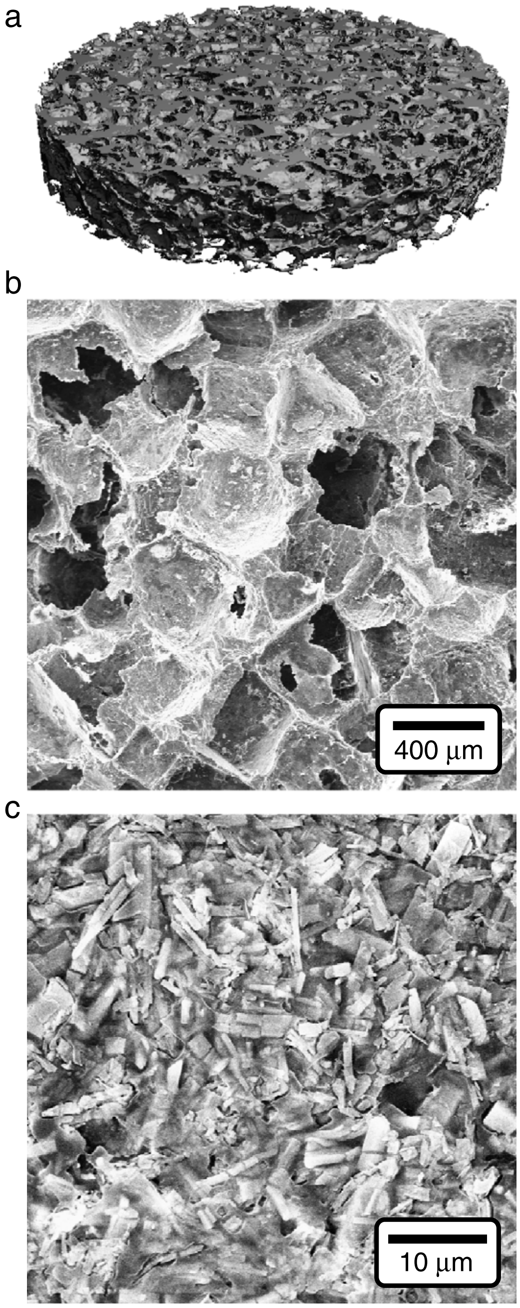

Fig. 1 – PEKK scaffolds molded at 375 °C with 75% porosity and 40 vol% HA whisker reinforcement, showing (a) a three-dimensional micro-computed tomography reconstruction of the scaffold architecture (10 mm diameter and 2 mm thick section), and SEM micrographs of (b) the scaffold microstructure and (c) HA whiskers exposed on the surface of scaffold struts.

The objective of this study was to investigate effects of the porosity, HA whisker reinforcement and mold temperature on the mechanical properties of PEKK scaffolds that were prepared using previously reported methods (Converse and Roeder, in press). The mechanical properties were evaluated in unconfined, uniaxial compression, using human trabecular bone as a benchmark for comparison.

2. Experimental methods

2.1. *Starting powders*

A commercially available PEKK powder (OXPEKK-C, Oxford Performance Materials, Enfield, CT) and a sodium chloride (NaCl) powder (Product No. 71382, Fluka, Switzerland) with mean particle sizes of approximately 70 and 600 μm, respectively, were used as-received. HA whiskers were synthesized using the chelate decomposition method as described in detail elsewhere (Roeder et al., 2003, 2006). Briefly, chemical solutions containing 0.1 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 randomly selected whiskers (Converse et al., 2007).

2.2. *Composite scaffold processing*

Composite scaffolds with 75%, 82.5% and 90% porosity were processed with 0, 20 or 40 vol% HA whisker reinforcement (Table 1). The total scaffold volume consisted of the desired pore volume plus the material volume. Thus, the reinforcement level was calculated based the desired material volume, while the porosity level was calculated based on the total scaffold volume, using the known density of each component ($\rho_{HA} = 3.1$, $\rho_{PEKK} = 1.31$ and $\rho_{NaCl} = 2.16$ g/cm^3). Note that the resultant scaffold porosity was measured in a prior study using micro-computed tomography which was further validated by paired measurements using Archimedes' principle (Converse and Roeder, in press).

Appropriate amounts of PEKK powder and HA whiskers were co-dispersed in ethanol using a sonic dismembrator (Model 500, Fisher Scientific, Pittsburgh, PA) at 20 kHz pulsed at 1.0 cycle/s while stirring at 1200 rpm. HA whiskers were first added to 2 mL of ethanol and ultrasonically dispersed for 1 min, followed by the addition of the PEKK powder and another 2 min of ultrasonic dispersion. After dispersion, the appropriate amount of the NaCl porogen was added to the suspension and mixed by hand using a spatula. Note that the total solids loading following the addition of the HA whiskers, PEKK powder and NaCl porogen corresponded to 50% by volume. After mixing, the viscous suspension was wet-consolidated using vacuum filtration, and the powder mixture was dried at 90 °C for at least 12 h to remove residual ethanol.

Composite scaffolds were prepared by compression molding and particle leaching. The dry powder mixture was densified at 125 MPa in a cylindrical die with a diameter of 10 mm using a manual hydraulic platen press (Model 3912, Carver Laboratory Equipment Inc., Wabash, IN). The die and densified powder mixture were then heated in a vacuum oven (−75 kPa) to the desired mold temperature and transferred back to the hydraulic platen press for compression molding at 250 MPa. Scaffolds with 82.5% and 90% porosity were molded at 350 °C, while scaffolds with 75% porosity were molded at 350, 365 and 375 °C (Table 1). After cooling to room temperature, the molded composite was ejected from the die and placed in approximately 300 mL deionized water for at least 72 h to dissolve the NaCl crystals. The deionized water bath was changed daily. As-molded composite scaffolds were 10 mm in diameter and 25 mm in height. Scaffolds processed at mold temperatures of 365 °C and 375 °C were lightly sanded with 600 grit SiC paper prior to particle leaching to remove an incomplete polymer skin layer that formed on the external surface of some as-molded scaffolds.

2.3. *Mechanical testing*

The mechanical properties of the composite scaffolds were investigated in un-confined, uniaxial compression. Note that the scaffold architecture was previously reported to be nearly isotropic (Converse and Roeder, in press). As-molded composite scaffolds were machined to a height of 10 mm using a low speed diamond wafer saw. Prior to testing, the scaffolds were soaked in phosphate buffered saline (PBS) at 37 °C for 16 h. Specimens were tested on an electromagnetic test instrument (ELF-3300, ElectroForce Systems Group, Bose Corp., Eden Prairie, MN) in PBS at 37 °C using a crosshead speed of 1 mm/min to 40% strain. Force–displacement data was used to calculate the apparent compressive elastic modulus (E), yield strength (YS) and yield strain (ε_y) of the composite scaffolds. Scaffold displacement was measured using a linear variable displacement transducer (LVDT) for apparent strain calculations. The elastic modulus was measured as the maximum slope using linear least squares regression to fit 20% segments of the stress–strain curve prior to the yield point. The yield point was determined by the intersection of the stress–strain curve with a 0.2% offset from the measured elastic modulus. The yield strain was measured after removing the toe region of the stress–strain curve by extrapolating the elastic modulus to zero stress.

2.4. *Scaffold microstructure*

Scaffold microstructure was examined by scanning electron microscopy (SEM) (Evo 50, LEO Electron Microscopy Ltd., Cambridge, UK) using an accelerating voltage of 10 or 20 kV and working distance of 10–20 mm. Scaffolds were notched with a razor blade and fractured in order to reveal the internal pore structure and strut cross-sections. All specimens were coated with Au–Pd by sputter deposition prior to electron microscopy.

Table 1 – Mechanical properties of HA whisker reinforced PEKK scaffolds, showing the mean (±standard deviation) apparent compressive elastic modulus (E), yield strength (YS) and yield strain (ε_y) of scaffolds with 75%, 82.5% and 90% porosity and 0, 20 and 40 vol% HA whisker reinforcement molded at 350, 365 and 375 °C.

Porosity (%)	HA content (vol%)	Mold temperature (°C)	E (MPa)	YS (MPa)	ε_y(%)
75	0	350	73.4 (11.1)	1.21 (0.16)	1.9 (0.3)
75	0	365	105.0 (12.3)	1.82 (0.22)	1.9 (0.2)
75	0	375	98.2 (10.7)	2.22 (0.25)	2.5 (0.2)
75	20	350	102.3 (12.0)	1.28 (0.13)	1.8 (0.8)
75	20	365	121.4 (14.4)	1.77 (0.30)	1.8 (0.2)
75	20	375	149.1 (39.2)	2.24 (0.42)	1.9 (0.3)
75	40	350	54.3 (18.3)	0.52 (0.17)	1.1 (0.1)
75	40	365	93.0 (43.6)	1.15 (0.38)	1.5 (0.2)
75	40	375	126.9 (30.1)	1.65 (0.34)	1.6 (0.3)
82.5	0	350	20.8 (4.6)	0.29 (0.10)	1.6 (0.5)
82.5	20	350	25.3 (7.9)	0.40 (0.13)	1.9 (0.6)
82.5	40	350	15.4 (5.4)	0.11 (0.02)	0.9 (0.3)
90	0	350	1.17 (0.16)	0.03 (0.01)	3.1 (1.6)
90	20	350	2.4 (0.9)	0.05 (0.02)	2.5 (0.9)
90	40	350	3.8 (1.6)	0.005 (0.002)	1.1 (0.2)

2.5. *Statistical methods*

Five scaffolds ($n = 5$) were prepared for each group based on porosity, HA content and mold temperature (Table 1). One-way analysis of variance (ANOVA) (JMP 5.1, StatView, SAS Institute, Inc., Cary, NC) was used to compare mechanical properties between experimental groups. Post hoc comparisons between porosity levels were performed using a Games–Howell test for unequal variances, and all other comparisons were performed using Tukey's HSD test, with a level of significance of 0.05. Two-way ANOVA was used to examine the effect and interaction of the porosity and reinforcement level on the mechanical properties of scaffolds molded at 350 °C, as well as the effect and interaction of the reinforcement level and mold temperature on the mechanical properties of scaffolds with 75% porosity. Non-linear least squares regression was used to correlate mechanical properties to the relative density, 1-(porosity/100), using a power-law.

3. Results

Fundamental differences were observed in the stress–strain behavior of the PEKK scaffolds depending on the porosity (Fig. 2(a)), HA content (Fig. 2(b)) and mold temperature (Fig. 2(c)). Unreinforced PEKK scaffolds with 75% porosity molded at 375 °C exhibited an initial linear increase in stress followed by a second linear region of lower slope (Fig. 2). All other scaffolds exhibited an initial linear increase in stress followed by a drop in stress and numerous subsequent reloading and localized failure events of varying magnitude (Fig. 2).

Effects of the scaffold porosity (75%, 82.5% and 90%) on the apparent compressive mechanical properties were investigated for scaffolds molded at 350 °C with 0, 20 and 40 vol% HA whisker reinforcement (Table 1, Fig. 2(a)). Increased porosity resulted in decreased elastic modulus and yield strength at each level of HA reinforcement ($p < 0.0001$, ANOVA) and differences between scaffolds at each level of porosity were statistically significant ($p < 0.05$, Games–Howell test) (Fig. 3). The magnitude of the elastic modulus and yield strength decreased by one and two orders of magnitude, respectively, for an increase from 75% to 90% porosity. Unreinforced scaffolds exhibited a greater relative decrease in modulus with increased porosity compared to reinforced scaffolds, while scaffolds reinforced with 40 vol% HA whiskers exhibited a greater relative decrease in yield strength with increased porosity compared to other groups (Fig. 3). The mean yield strain ranged from 0.9% to 3.1% and exhibited no trends with the scaffold porosity, but decreased with increased HA reinforcement at each level of porosity ($p < 0.05$, ANOVA) (Table 1).

Effects of HA whisker reinforcement (0, 20 and 40 vol%) on the apparent compressive mechanical properties were investigated for scaffolds molded at 350 °C with 75%, 82.5% and 90% porosity (Fig. 3), and scaffolds molded at 350, 365 and 375 °C with 75% porosity (Table 1, Fig. 2(b)). The elastic modulus reached a maxima at 20 vol% HA reinforcement for scaffolds molded at 350 °C with 75% and 82.5% porosity (Fig. 3(a)), and scaffolds molded at 350, 365 and 375 °C with 75% porosity (Fig. 4(a)), though differences were not always statistically significant. In contrast, scaffolds with 90% porosity molded at 350 °C exhibited a continued increase in modulus with increased HA reinforcement up to 40 vol% (Fig. 3(a)). Differences in the yield strength between scaffolds with 0 and 20 vol% HA were not statistically significant, but scaffolds with 40 vol% HA exhibited decreased yield strength ($p < 0.05$, Tukey's HSD test), for a given level of porosity (Fig. 3(b)) or mold temperature (Fig. 4(b)). Scaffolds with 40 vol% HA reinforcement exhibited a decreased yield strain (Table 1) compared to other groups overall ($p < 0.01$, ANOVA), but differences between groups for a given level of porosity or mold temperature were not always statistically significant.

Effects of the mold temperature (350, 365 and 375 °C) on the apparent compressive mechanical properties were investigated for scaffolds with 75% porosity and 0, 20 and 40 vol% HA whiskers (Table 1, Fig. 2(c)). Increased mold temperature resulted in increased elastic modulus ($p < 0.0001$, ANOVA) (Fig. 4(a)), yield strength ($p < 0.0001$, ANOVA) (Fig. 4(b)), and yield strain ($p < 0.01$, ANOVA) (Table 1). These trends were also statistically significant for each level of HA reinforcement ($p < 0.05$, ANOVA), except for the yield strain in scaffolds reinforced with 20 vol% HA. The relative increase in the

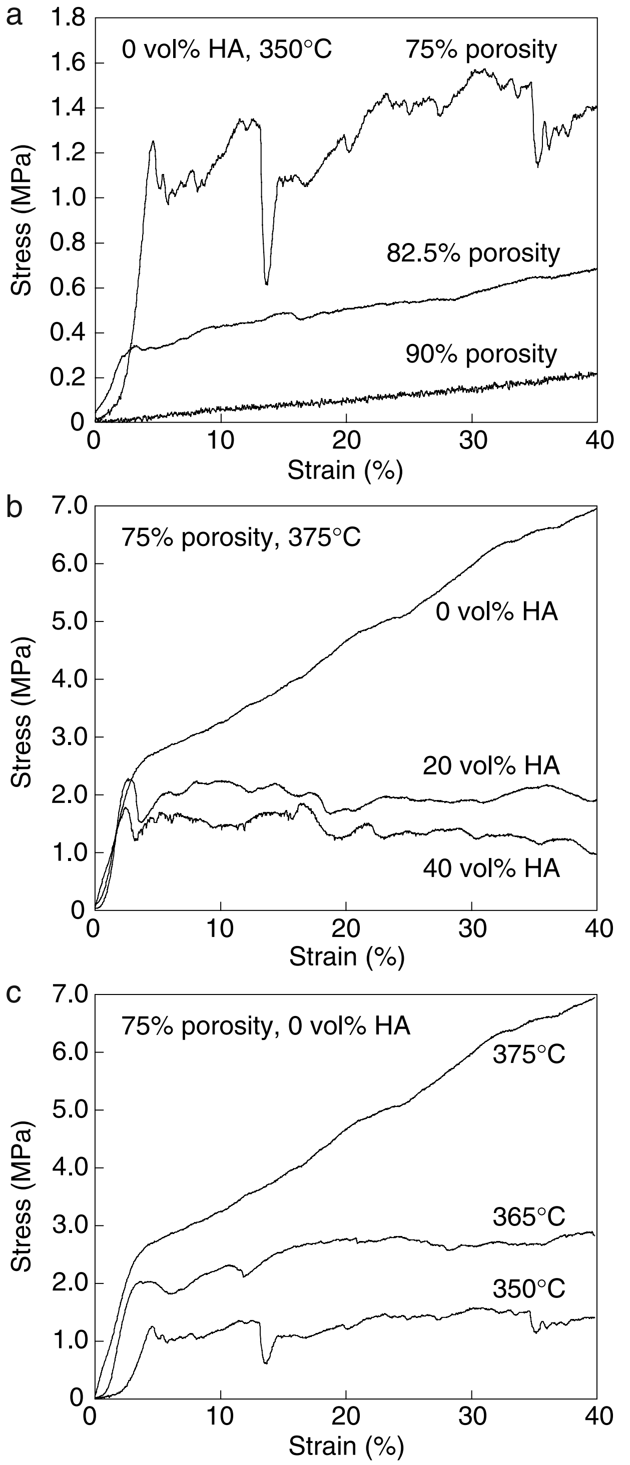

Fig. 2 – Representative stress–strain curves for unconfined, uniaxial compression of HA whisker reinforced PEKK scaffolds showing the effects of (a) porosity in unreinforced PEKK scaffolds molded at 350 °C, (b) HA reinforcement in scaffolds molded at 375 °C with 75% porosity, and (c) mold temperature in unreinforced scaffolds with 75% porosity. The median specimen is shown for each group based on the yield strength. Note that scaffold densification occurred at strains greater than those plotted in this figure and scaffolds with 90% porosity exhibited an initial linear region and elastic limit that was below the scale of the figure in (a).

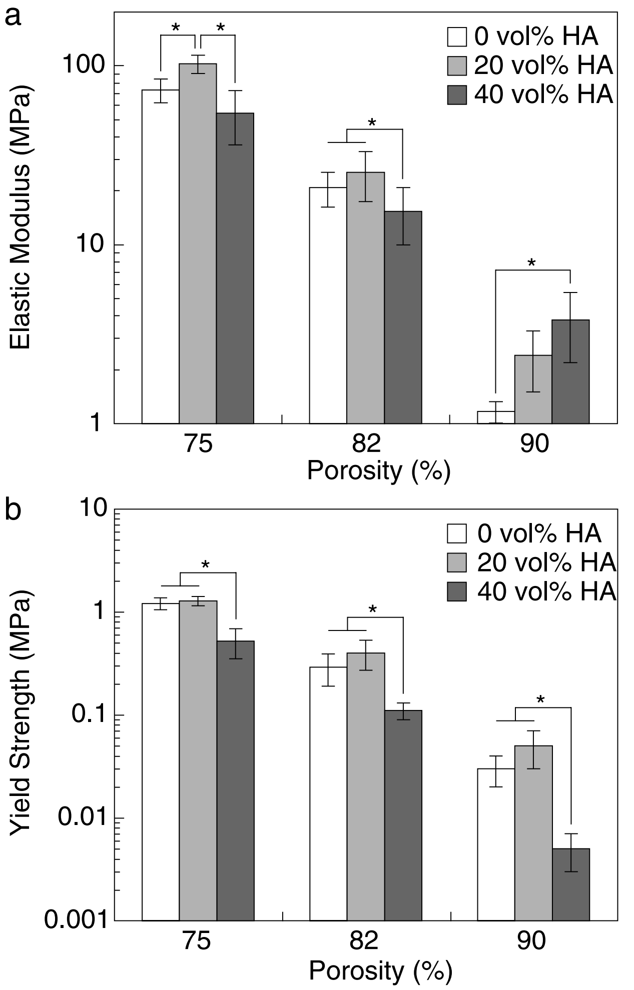

Fig. 3 – The apparent compressive (a) elastic modulus and (b) yield strength of HA whisker reinforced PEKK scaffolds showing the effects of porosity on scaffolds molded at 350 °C with 0, 20 and 40 vol% HA whiskers. All differences between groups with the same level of HA reinforcement but different levels of porosity were statistically significant ($p < 0.05$, Games–Howell test). Asterisks denote statistically significant differences between groups with the same porosity but different levels of HA reinforcement ($p < 0.05$, Tukey's HSD test).

elastic modulus and yield strength for an increase in mold temperature became more prominent with increased HA content (Fig. 4). The magnitude of the elastic modulus and yield strength in scaffolds reinforced with 40 vol% HA increased more than two- and three-fold, respectively, for an increase in mold temperature from 350 to 375 °C.

4. Discussion

4.1. *Comparisons to human trabecular bone*

The apparent, compressive mechanical properties of HA whisker reinforced PEKK scaffolds were within the range reported for human vertebral trabecular bone (Table 2).

Table 2 – Comparison of the apparent compressive elastic modulus (*E*), yield strength (YS) and yield strain (ε_y) measured for HA whisker reinforced PEKK scaffolds compared to human trabecular bone from the proximal tibia and vertebra (Keaveny et al., 2001; Kopperdahl and Keaveny, 1998; Morgan and Keaveny, 2001).

	Porosity (%)	Apatite content (vol%)	*E* (MPa)	YS (MPa)	ε_y (%)
Human trabecular bone (proximal tibia)	~80–95	~40	200–2000	2–12	0.7–1.2
Human trabecular bone (vertebra)	~80–95	~40	20–500	0.5–4	0.7–1.0
HA whisker reinforced PEKK scaffolds	75–90	0–40	1–190	0.002–2.7	0.7–3.8

Scaffolds with 75% porosity and 20 vol% HA molded at 375 °C exhibited a mean elastic modulus and yield strength of 149 MPa and 2.2 MPa, respectively, which was the highest of the conditions investigated in this study and similar to human vertebral trabecular bone. Moreover, the elastic modulus was greater than 50 MPa, and the yield strength was greater than 0.5 MPa, for scaffolds with 75% porosity at all combinations of reinforcement level and mold temperature (Table 1, Fig. 4). The mean yield strain of scaffolds reinforced with 40 vol% HA and molded at 350 °C with 75%, 82.5% or 90% porosity was within the range reported for human trabecular bone (Table 1). The yield strain of scaffolds prepared under all other conditions exceeded that of human trabecular bone.

The ability to mimic the apparent compressive mechanical properties of human vertebral trabecular bone was not without limitation. The mechanical properties achieved by scaffolds with 75% porosity were similar to those of vertebral trabecular bone with 90%–95% porosity. The apparent elastic modulus and yield strength of scaffolds with 90% porosity were significantly lower than those of human trabecular bone (Tables 1 and 2). Thus, the scaffolds in this study did not mimic the mechanical properties human vertebral trabecular bone at a similar level of porosity and a design trade-off may exist between sufficient mechanical integrity and porosity for bone ingrowth. However, the effects of the HA reinforcement level and mold temperature were not studied in detail at greater than 75% porosity. Moreover, 75% porosity has been sufficient for bone ingrowth in other scaffold materials (Karageorgiou and Kaplan, 2005; Ryan et al., 2006). Scaffolds with 75% porosity exhibited interconnected porosity and a mean pore size in the range 200–300 μm (Converse and Roeder, in press) (Fig. 1), which is known to be favorable for osteointegration (Karageorgiou and Kaplan, 2005; Ryan et al., 2006). Therefore, future work should investigate bone ingrowth into HA whisker reinforced PAEK scaffolds.

The ability to tailor the mechanical properties of HA whisker reinforced PEKK scaffolds may be more important than mimicking a particular tissue, due to the wide variation in mechanical properties exhibited by trabecular bone. The mean elastic modulus and yield strength increased by one and two orders of magnitude, respectively, for a decrease in porosity from 90% to 75% at a given HA reinforcement level and mold temperature. More importantly, even at a fixed level of porosity (75%), the mean elastic modulus and yield strength ranged from 54–149 and 0.52–2.24 MPa, respectively, due to changes in the HA reinforcement level and mold temperature. Therefore, the scaffold mechanical properties were able to be tailored independent of any one parameter, such as porosity, which may need to be fixed for other design constraints. Moreover, other parameters, such as the porogen size, HA whisker size and aspect ratio, and polymer crystallinity were not investigated in this study.

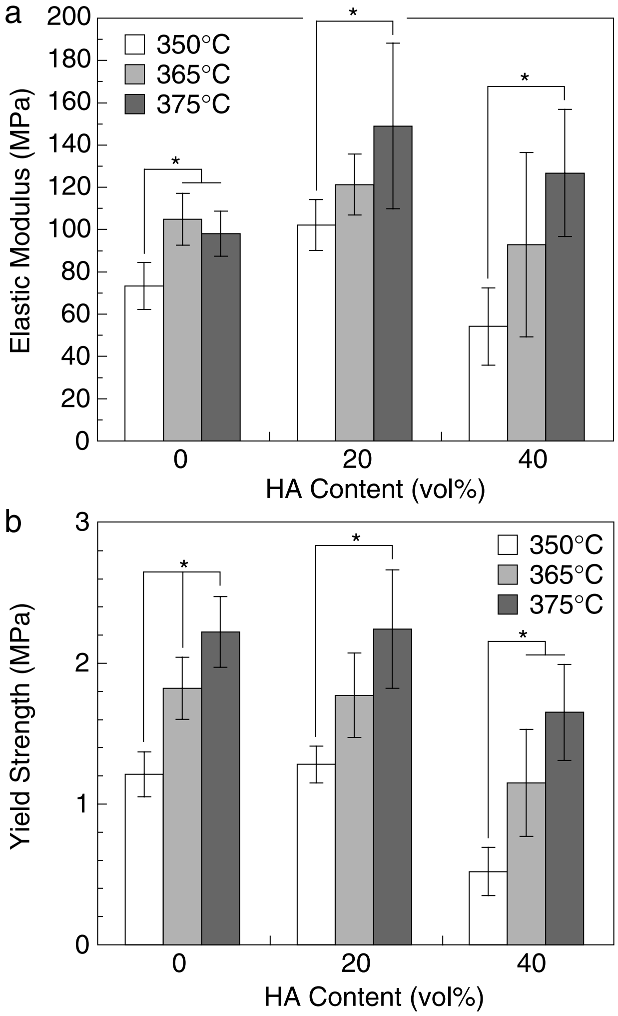

Fig. 4 – The apparent compressive (a) elastic modulus and (b) yield strength of HA whisker reinforced PEKK scaffolds showing the effects of the HA content and mold temperature on scaffolds with 75% porosity. The elastic modulus reached a maxima at 20 vol% HA reinforcement for scaffolds though differences at a given mold temperature were not always statistically significant. Differences in yield strength between scaffolds with 0 and 20 vol% HA were not statistically significant, but scaffolds with 40 vol% HA exhibited decreased yield strength, at a given mold temperature. Asterisks denote statistically significant differences between groups with the same level of HA reinforcement but different levels of the mold temperature ($p < 0.05$, Tukey's HSD test).

Table 3 – Linear least squares regression of the apparent compressive elastic modulus (E) and yield strength (YS) and with the relative density (ρ) using a power-law, $y = A \cdot \rho^b$. The data set included all specimens molded at 350 °C. Note that the yield strain (ε_y) was not correlated with the relative density.

HA content (vol%)	E (MPa)				YS (MPa)			
	A	b	p	R^2	A	b	p	R^2
0	45,500	4.55	<0.0001	0.98	307	4.01	<0.0001	0.97
20	34,800	4.19	<0.0001	0.97	225	3.70	<0.0001	0.95
40	2,590	2.25	<0.0001	0.89	611	5.06	<0.0001	0.96

4.2. *Stress–strain behavior*

PEKK and HA whisker reinforced PEKK scaffolds exhibited stress–strain behavior similar to that of an elastic–brittle foam, with the possibility of concomitant plasticity in the polymer phase, regardless of the level of porosity, HA reinforcement or mold temperature (Fig. 2). Elastic–brittle and elastic–plastic foams are characterized by an initial linear increase in stress due to elastic bending of the scaffold struts, followed by an elastic limit and drop in stress due to elastic buckling, plastic yielding, and/or brittle fracture of scaffold struts (Gibson and Ashby, 1997). Brittle behavior was predominate in HA reinforced scaffolds, evidenced by a sharp drop in stress followed by numerous reloading and localized failure events in the plateau region (Fig. 2). In contrast, human trabecular bone exhibits elastic–plastic behavior in compression.

4.3. *Effects of porosity*

Increased porosity resulted in a non-linear decrease in the apparent elastic modulus and yield strength for both reinforced and unreinforced PEKK scaffolds (Fig. 3), as expected. After converting the porosity to a relative density, the increase in elastic modulus and yield strength with increased relative density followed a power-law (Table 3), similar to trabecular bone and other open-cell foams. In trabecular bone, the exponential term has been measured in the range 1.5–2.25 for either the compressive modulus or yield strength, depending on the tissue source (Keaveny et al., 2001; Morgan and Keaveny, 2001). Note that decreased relative density corresponded not only to a linear loss in the volume of material, but also non-linear changes in the scaffold architecture. Previous measurements using micro-computed tomography revealed that decreased relative density corresponded to a non-linear decrease in scaffold strut thickness and a linear increase in the structure model index, where the latter indicates a change in strut morphology from plate-like to rod-like (Converse and Roeder, in press).

4.4. *Effects of HA whisker reinforcement*

Increased HA whisker reinforcement generally resulted in an increased elastic modulus from 0 to 20 vol% HA and a subsequent decrease from 20 to 40 vol% HA (Figs. 3(a), 4(a)). Thus, the elastic modulus was greatest overall for scaffolds reinforced with 20 vol% HA whiskers (Fig. 4(a)). The yield strength was decreased in scaffolds with 40 vol% HA compared to those with 0 or 20 vol% HA regardless of the level of porosity and mold temperature (Figs. 3(b) and 4(b)). Previous studies of HA reinforced degradable polymer scaffolds also reported decreased elastic modulus and strength at high reinforcement levels (Causa et al., 2006; Thomson et al., 1998). The behavior was attributed to increased interaction or contact between reinforcement particles within the polymer matrix at high volume fractions (Thomson et al., 1998). Additionally, dense HA-polymer composites have also exhibited decreased yield or tensile strength with increased reinforcement as HA particles acts as "flaws" in the polymer matrix due to poor interfacial bonding (Roeder et al., 2008). Therefore, an important design trade-off may exist as increased levels of HA provide added bioactivity, but loss of mechanical strength (Kurtz and Devine, 2007; Roeder et al., 2008).

For the reasons above, the elastic modulus was similar for scaffolds with 0 and 40 vol% HA at a given mold temperature or porosity, except for scaffolds molded at 350 °C with 90% porosity, where the modulus of scaffolds with 40 vol% HA was increased by approximately 60% over unreinforced scaffolds (Fig. 3(a)). There was no clear explanation for the latter behavior, but a couple reasons may be speculated. Unreinforced scaffolds with 90% porosity were observed to exhibit a more discontinuous strut morphology compared to HA reinforced scaffolds, whereas no such differences were observed at lower levels of porosity (Converse and Roeder, in press). Therefore, the presence of HA whiskers may have improved the integrity of scaffold struts by increasing the melt viscosity and/or reinforcing the viscous melt during molding. Also, as the strut thickness decreased with increased porosity, approaching the length of the HA whiskers, the whiskers may have become more aligned within the plane of the strut.

The HA whiskers used in the this study have previously been shown to result in improved mechanical properties compared to an equiaxed HA powder (Kane et al., 2008; Roeder et al., 2003, 2008) despite the fact that the whisker aspect ratio does experience degradation during molding, decreasing by approximately 50% (Yue and Roeder, 2006). The amount of whisker degradation was not measured for the scaffolds prepared in this study and will therefore be an important question for further study.

4.5. *Effects of mold temperature*

Increased mold temperature resulted in an increased apparent elastic modulus, yield strength and yield strain (Fig. 4, Table 1). These trends suggest that an increased mold temperature improved sintering of the polymer powder, and therefore integration of HA whisker reinforcements in the polymer

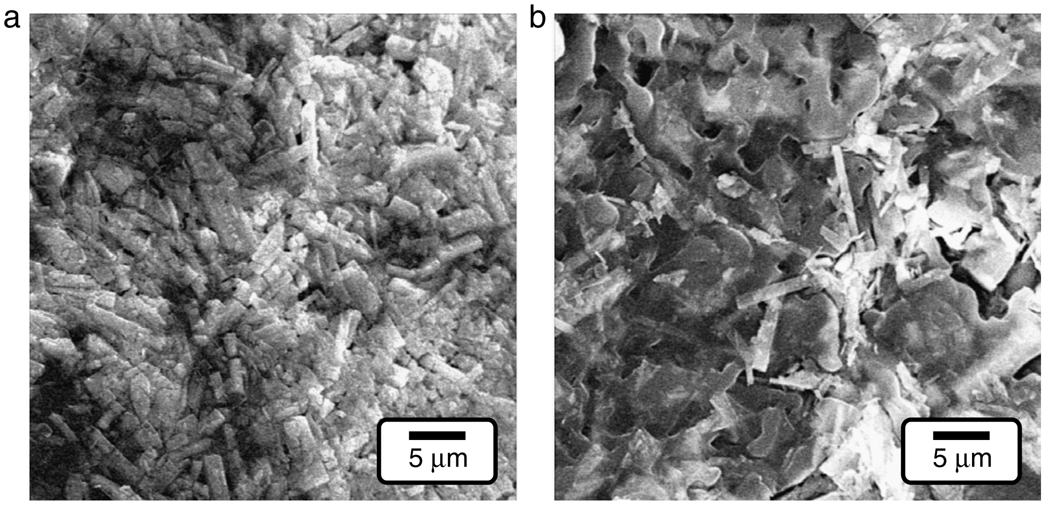

Fig. 5 – SEM micrographs of PEKK scaffolds with 75% porosity and 40 vol% HA whisker reinforcement showing decreased consolidation of the PEKK matrix, but greater exposure of HA whiskers the surface of struts in scaffolds molded at (a) 350 °C **compared to (b)** 375 °C.

matrix, during compression molding. This explanation is supported by the observed transition in the stress–strain curves of unreinforced scaffolds from elastic–brittle to elastic–plastic with increased mold temperature (Fig. 2(c)). Moreover, the relative increase in the elastic modulus and yield strength for an increase in mold temperature became more prominent with increased HA content, suggesting that an increased mold temperature was partly able to mitigate the decreased mechanical properties associated with an increase of 20 to 40 vol% HA (Fig. 4). SEM observation of scaffold strut surfaces verified increased sintering of the polymer matrix with increased mold temperature (Fig. 5). However, HA reinforcements were also more encapsulated by the polymer matrix, or less exposed on scaffold strut surfaces, with increased mold temperature. Exposed HA particles provide sites for protein adsorption, cell attachment and apposition of new bone tissue (Converse and Roeder, in press), which may improve osteointegration of polymer scaffolds. Therefore, increased mold temperature may compromise the biological function of HA reinforcements and should be further investigated *in vitro*. Also, note that further increases in the mold temperature beyond those employed in this study could lead to oxidation of the polymer.

The polymer crystallinity may have also contributed to the increased elastic modulus and yield strength with increased mold temperature. An increased mold temperature increased the duration of time required to cool the PEKK scaffold and mold to the glass transition temperature (163 °C) after compression molding, which would be expected to increase the polymer crystallinity. Increased crystallinity in PEEK has been shown to result in decreased ductility but increased elastic modulus and tensile strength (Gao and Kim, 2000).

5. Conclusions

The apparent mechanical properties of porous hydroxyapatite (HA) whisker reinforced polyetherketoneketone (PEKK) scaffolds – prepared at various levels of porosity (75%, 82.5% and 90%), HA content (0, 20 and 40 vol%) and mold temperature (350, 365 and 375 °C) – were investigated in unconfined, uniaxial compression, using human trabecular bone as a benchmark for comparison:

(1) Increased porosity resulted in a non-linear decrease in the elastic modulus and yield strength for both reinforced and unreinforced PEKK scaffolds, as expected. The increase in elastic modulus and yield strength with increased relative density followed a power-law, similar to trabecular bone and other open-cell foams.
(2) Increased HA reinforcement resulted in an increased elastic modulus from 0 to 20 vol% HA and a subsequent decrease from 20 to 40 vol% HA. Thus, the elastic modulus was greatest overall for scaffolds reinforced with 20 vol% HA whiskers. Increased HA reinforcement resulted in decreased yield strength and strain.
(3) Increased mold temperature resulted in an increased elastic modulus, yield strength and yield strain, due to improved sintering of the PEKK powder.
(4) The apparent mechanical properties were tailored to mimic human trabecular bone. The elastic modulus was greater than 50 MPa, and the yield strength was greater than 0.5 MPa, for scaffolds with 75% porosity at all combinations of reinforcement level and mold temperature. Scaffolds with 75% porosity and 20 vol% HA molded at 375 °C exhibited a mean elastic modulus and yield strength of 149 MPa and 2.2 MPa, respectively, which was the highest of the conditions investigated in this study and similar to human vertebral trabecular bone.

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