Effects of the mold temperature on the mechanical properties and crystallinity of hydroxyapatite whisker-reinforced polyetheretherketone scaffolds

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Abstract: Porous and bioactive polyetheretherketone (PEEK) scaffolds have potential to replace metallic scaffolds for biologic fixation of permanent implants adjacent to trabecular bone, such as interbody spinal fusion devices. The objective of this study was to investigate the effects of the mold temperature and PEEK powder on the mechanical properties and crystallinity of hydroxyapatite (HA) whisker-reinforced PEEK scaffolds prepared using compression molding and porogen leaching. Scaffolds were prepared at mold temperatures ranging 340–390°C with a 50 or 10 μm PEEK powder, 75 vol% porosity, and 20 vol% HA whiskers. Scaffold mechanical properties were evaluated in unconfined, uniaxial compression and the PEEK matrix crystallinity was measured using specular reflectance Fourier transform infrared spectroscopy. Increased mold temperature resulted in increased compressive modulus, yield strength, and yield strain, reaching a plateau at ~370°C. HA reinforcements were observed to be segregated between PEEK particles, which inhibited PEEK particle coalescence during compression molding at temperatures less than 365°C but also ensured that bioactive HA reinforcements were exposed on scaffold strut surfaces. Increased mold temperature also resulted in decreased PEEK crystallinity, particularly for scaffolds molded at greater than 375°C. The PEEK powder size exhibited relatively minor effects on the scaffold mechanical properties and PEEK crystallinity. Therefore, the results of this study suggested that HA-reinforced PEEK scaffolds should be compression molded at 370–375°C. The apparent compressive modulus, yield strength, and yield strain for scaffolds molded at 370–375°C was 75–92 MPa, 2.0–2.2 MPa, and 2.5–3.6%, respectively, which was within the range exhibited by human vertebral trabecular bone. © 2013 Wiley Periodicals, Inc. J Biomed Mater Res Part B: Appl Biomater 101B: 576–583, 2013.

Key Words: biocomposite, crystallinity, hydroxyapatite, mechanical properties, polyetheretherketone, scaffold, whisker

INTRODUCTION

Polyaryletherketones (PAEKs), such as polyetheretherketone (PEEK), are high-performance semicrystalline thermoplastic polymers capable of replacing metals in load-bearing orthopedic and spinal implants due to demonstrated biocompatibility, safety, and biomechanical properties.[1–4] For example, PEEK has been used in place of metals for interbody spinal fusion cages. The radiolucency of PEEK enables improved postoperative radiographic assessment of fusion by eliminating radiographic artifacts caused by metallic scaffolds and implants.[5–7] The elastic modulus of PEEK enables improved transfer of osteogenic strains to bone tissue forming within the cage while minimizing contact stresses which could lead to subsidence.[8] However, osteointegration of current PEEK implants may be limited by fibrous tissue encapsulation due to a lack of bioactivity for direct apposition of bone tissue[1,9–11] and a lack of porosity for bone ingrowth.[12]

Bioactive polymer composites can be readily prepared by the inclusion of a bioactive filler or reinforcement, such as hydroxyapatite (HA).[13,14] Therefore, a number of studies over the last decade began to investigate bioactive PAEK composites, and these are reviewed in detail elsewhere.[11] Dense HA-reinforced PEEK composites have been engineered to exhibit mechanical properties similar to those of human cortical bone.[15–17] The bioactivity of HA-reinforced PEEK was confirmed *in vitro* after immersion in simulated body fluid.[18] After implantation in a porcine cranial defect for 16 weeks, beta-tricalcium phosphate (β-TCP)-reinforced PEEK exhibited a greater pushout strength compared with PEEK alone, due to direct bone apposition to the β-TCP reinforcements but not the PEEK matrix.[10]

Porous HA-reinforced PAEK scaffolds have been prepared by selective laser sintering[19,20] or compression molding and porogen leaching.[21,22] Compression molding and porogen leaching was recently shown to enable the preparation of polyetherketoneketone (PEKK) scaffolds comprising 75–90% porosity and 0–40 vol% HA whisker reinforcements.[21,22] The scaffold architecture and microstructure exhibited characteristics known to be favorable for osteointegration: scaffold porosity was interconnected with a mean pore size of 200–300 μm while bioactive HA reinforcements were both exposed on strut surfaces and embedded in the PEKK matrix.[21] Scaffolds with 75% porosity and 20 vol% HA whisker reinforcement molded at 375°C exhibited the highest compressive modulus (149 MPa) and yield strength (2.2 MPa), which were comparable with the properties of human vertebral trabecular bone.[22]

The objective of this study was to investigate the effects of the mold temperature and PEEK powder on the mechanical properties and crystallinity of HA whisker-reinforced PEEK scaffolds prepared using compression molding and porogen leaching. PEEK powders were used instead of the PEKK powder used in previous investigations due to current clinical use in implantable devices and the availability of powders with different particle size. In previous work, the mechanical properties of HA whisker-reinforced PEKK improved with increased mold temperatures of 350, 365, and 375°C,[22] but the optimum mold temperature was not determined. Moreover, the processing temperature and presence of reinforcement phases are also known to influence the crystallinity of PEEK and thus the mechanical properties,[23–25] but the crystallinity of HA-reinforced PEEK scaffolds has not been previously investigated.

MATERIALS AND METHODS
Starting powders
Commercially available PEEK powders, LT1PF and LT3UF (PEEK-OPTIMA, Invibio, West Conshohocken, PA), with a median particle diameter of 50 and 10 μm, respectively, and number average molecular weight of 115,000 and 83,000, respectively, were used as-received. A sodium chloride (NaCl) porogen (Product No. 71382, Fluka, Switzerland) with a mean particle size of ∼600 μm was also used as-received. HA whiskers were synthesized using the chelate decomposition method as described in detail elsewhere.[26,27] Briefly, chemical solutions containing 0.1 M lactic acid (Sigma–Aldrich, St. Louis, MO), 0.03 M phosphoric acid (Sigma–Aldrich), and 0.05 M calcium hydroxide (Aldrich Chemical Company, 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 log-normal distribution for a sample of 500 randomly selected whiskers.[16]

Scaffold processing
PEEK scaffolds were prepared comprising 75 vol% porosity and 20 vol% HA whisker reinforcements. Appropriate amounts of the LT1PF or LT3UF PEEK 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 cycles/s while stirring at 1200 rpm. HA whiskers were first added to 2.4 mL of ethanol and ultrasonically dispersed for 1 min, followed by the addition of the PEEK powder and another 2 min of ultrasonic dispersion. Ethanol was used as a dispersant to minimize dissolution of the NaCl porogen and for rapid evaporation. After dispersion, the appropriate amount of NaCl porogen, was added to the suspension and mixed by hand using a spatula. The total solids content of the PEEK powder, HA whiskers, and NaCl porogen in the ethanol dispersant was ∼50 vol%. 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 porogen leaching. The dry powder mixture was densified at 125 MPa in a 10 mm diameter cylindrical die using a manual hydraulic platen press (Model 3912, Carver Laboratory Equipment, Wabash, IN). The die and densified powder mixture were then heated in a vacuum oven to the desired mold temperature and transferred back to the hydraulic press for compression molding at 250 MPa. The mold temperature was varied from 340 to 390°C in 5°C increments. After cooling to ambient temperature, the molded composite was ejected from the die and placed in approximately 300 mL deionized (DI) water for at least 72 h to leach out the NaCl porogen. The DI water bath was changed daily. As-molded composites were 10 mm in diameter and 25 mm in height. A 1 mm section from the top and bottom surfaces was removed and discarded. Scaffolds were lightly sanded with 600 grit SiC paper before particle leaching to remove an impermeable polymer film from the external surface of some as-molded scaffolds. Five scaffolds ($n = 5$) were prepared for each experimental group based on the mold temperature and PEEK powder.

Mechanical testing
The mechanical properties of the composite scaffolds ($n = 5$/group) were investigated in unconfined, uniaxial compression using methods adapted from ASTM D 1621.[28] Test specimens were sectioned to a height of 10 mm from the bottom half of the as-molded scaffold using a low speed diamond wafer saw and soaked in phosphate-buffered saline (PBS) at 37°C for at least 16 h before testing. Specimens were loaded using an electromagnetic test instrument (ELF-3300, ElectroForce Systems Group, Bose Corp., Eden Prairie, MN) in PBS at 37°C with 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. Note that although some experimental groups exhibited behavior indicative of an elastic collapse stress and strain rather than a yield point, yield stress and strain were
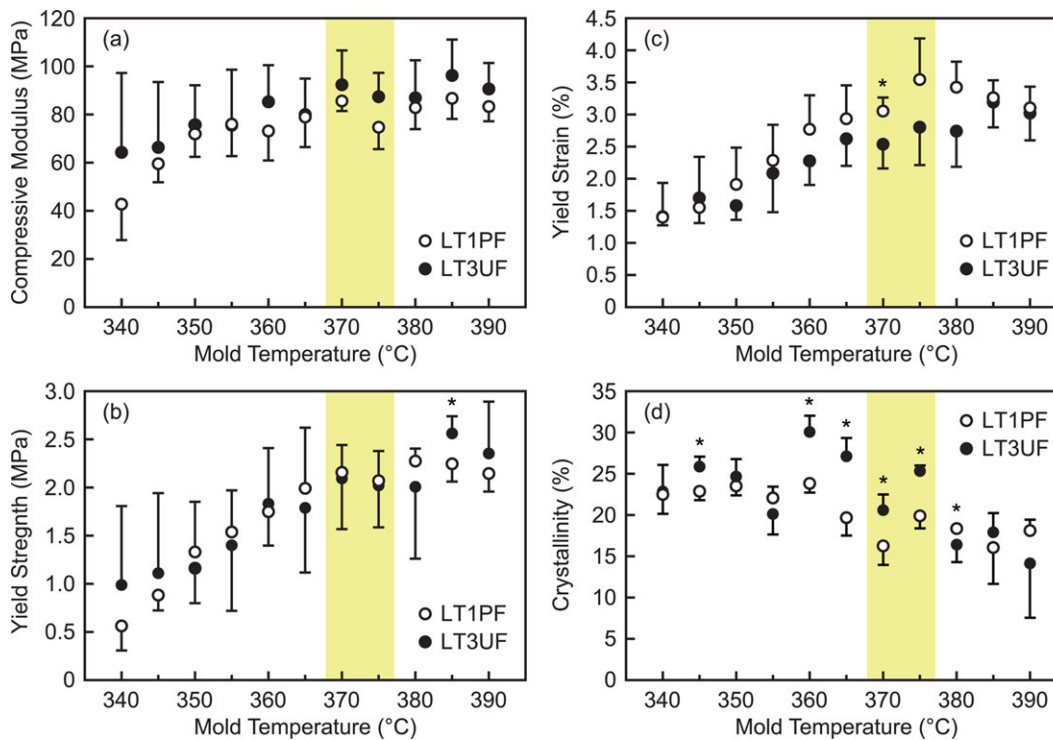
FIGURE 1. Effects of the mold temperature and PEEK powder (LT1PF vs. LT3UF) on the (a) compressive modulus, (b) compressive yield strength, (c) compressive yield strain, and (d) PEEK crystallinity of scaffolds comprising 75% porosity and 20 vol% HA whisker reinforcement. Error bars show one standard deviation of the mean. Asterisks indicate a statistically significant difference between PEEK powders at a given mold temperature ($p < 0.05$, Tukey). Differences between mold temperatures are shown in Table I. The temperature range concluded to be optimal is shaded. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

used for consistency. Apparent strains were calculated from the platen displacement measured using a linear variable displacement transducer. The elastic modulus was measured using linear least squares regression as the maximum slope of any portion of the stress–strain curve before the yield point and spanning at least 20% of the yield strain. The yield strength 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.

Microscopy

Scaffolds exhibiting the median yield strength for each experimental group were examined by scanning electron microscopy (SEM). Fracture specimens were sectioned to a height of ~4 mm from the top of as-molded scaffolds, notched with a razor blade, and fractured to reveal the internal scaffold architecture and strut surfaces. In order to examine the internal scaffold microstructure, polished specimens were prepared from the remaining portion of as-molded scaffolds located in between mechanical testing and fracture surface specimens. Specimens were embedded in transparent polymethylmethacrylate (Aldrich Chemical Company, Milwaukee, WI) under vacuum, sectioned with a low speed diamond wafer saw, and polished with a series of abrasives beginning with 600 grit SiC paper and ending

with 1 μm diamond paste. Fracture surfaces and polished sections were coated with Ir by sputter deposition and examined using a SEM (Evo 50, LEO Electron Microscopy, Cambridge, UK) at an accelerating voltage of 20 kV and working distance of 5–10 mm.

Crystallinity

The crystallinity of the PEEK matrix was measured for scaffolds exhibiting the median yield strength for each experimental group. Polished sections were prepared from the center of each scaffold and adjacent to mechanical testing specimens using the methods described above. Crystallinity was measured using specular reflectance Fourier transform infrared (R-FTIR) spectroscopy following ASTM F2778.[29] Absorbance was measured over wavenumbers from 900 to 1400 cm^{-1} using a 50 μm^2 aperture focused on scaffold struts within the polished cross section. Percent crystallinity (X_C) was measured as

$$X_C = \frac{CI - 0.728}{1.549} \cdot 100 \qquad (1)$$

where CI is the peak height at a wavenumber of 1305 cm^{-1} divided by the peak height at a wavenumber of 1280 cm^{-1}. The PEEK crystallinity for each scaffold was measured as the mean (±standard deviation) of 10 measurements evenly distributed across the scaffold cross-section. Note that a pilot study confirmed that crystallinity measurements

TABLE I. Effects of the Mold Temperature (T_{mold}) and PEEK Powder (LT1PF vs. LT3UF) on the Mean (±Standard Deviation) Compressive Modulus (*E*), Compressive Yield Strength (*YS*), Compressive Yield Strain (ε_y), and PEEK Crystallinity (X_C) of Scaffolds Comprising 75% Porosity and 20 vol% HA Whisker Reinforcement

T_{mold} (°C)	LT1PF PEEK Powder				LT3UF PEEK Powder			
	E (MPa)	*YS* (MPa)	ε_y (%)	X_C (%)	*E* (MPa)	*YS* (MPa)	ε_y (%)	X_C (%)
340	42.8 (14.9)[a]	0.56 (0.25)[a]	1.41 (0.14)[a]	23 (2)[abc]	64.3 (32.9)[a]	0.98 (0.82)[a]	1.41 (0.51)[a]	23 (3)[bcd]
345	59.5 (7.7)[ab]	0.88 (0.16)[ab]	1.56 (0.25)[a]	23 (1)[ab]	66.3 (27.2)[a]	1.11 (0.83)[ab]	1.71 (0.63)[ab]	26 (1)[ab]
350	71.9 (9.5)[bc]	1.33 (0.52)[bc]	1.92 (0.56)[ab]	24 (1)[a]	75.7 (16.4)[a]	1.16 (0.36)[ab]	1.59 (0.23)[abc]	25 (2)[bc]
355	76.0 (13.3)[bc]	1.54 (0.43)[bcd]	2.29 (0.54)[abc]	22 (1)[abc]	75.6 (23.1)[a]	1.40 (0.68)[abc]	2.09 (0.62)[abcd]	20 (3)[de]
360	73.1 (12.2)[bc]	1.75 (0.35)[cd]	2.78 (0.52)[bcd]	24 (1)[a]	85.3 (15.2)[a]	1.83 (0.58)[abc]	2.28 (0.39)[abcde]	30 (2)[a]
365	78.9 (12.5)[bc]	1.99 (0.63)[cd]	2.94 (0.51)[cd]	20 (2)[cd]	80.0 (14.9)[a]	1.79 (0.67)[abc]	2.63 (0.43)[bcde]	27 (2)[ab]
370	85.6 (4.17)[c]	2.16 (0.28)[d]	3.06 (0.20)[cd]	16 (2)[e]	92.4 (14.2)[a]	2.09 (0.53)[abc]	2.54 (0.39)[bcde]	21 (2)[cde]
375	74.7 (9.1)[bc]	2.07 (0.31)[cd]	3.55 (0.63)[d]	20 (2)[bcd]	87.4 (9.9)[a]	2.02 (0.44)[abc]	2.81 (0.60)[de]	25 (1)[b]
380	83.9 (8.9)[c]	2.27 (0.13)[d]	3.43 (0.39)[d]	18 (1)[de]	86.9 (15.6)[a]	2.01 (0.75)[abc]	2.75 (0.57)[be]	16 (2)[ef]
385	86.7 (8.5)[c]	2.25 (0.18)[d]	3.27 (0.26)[d]	16 (4)[e]	96.2 (14.9)[a]	2.56 (0.18)[c]	3.20 (0.41)[e]	18 (2)[ef]
390	83.3 (6.1)[c]	2.14 (0.19)[d]	3.11 (0.32)[cd]	18 (1)[de]	90.6 (10.8)[a]	2.35 (0.54)[bc]	3.03 (0.44)[de]	14 (7)[f]

Differences between mold temperatures not connected by the same letter were statistically significant ($p < 0.05$, Tukey). The temperature range concluded to be optimal is shaded.

within an experimental group were not influenced by the sampling location within scaffolds ($p > 0.7$ analysis of variance (ANOVA)).

Statistical methods

Effects of the mold temperature and PEEK powder on the compressive mechanical properties and crystallinity of scaffolds were examined using one- and two-way ANOVA (JMP 9.0, SAS Institute, Cary, NC). *Post hoc* comparisons were performed using Tukey's HSD test. The level of significance for all tests was $p < 0.05$.

RESULTS

The compressive modulus, yield strength, and yield strain of scaffolds prepared with both the LT1PF or LT3UF PEEK powders increased with increased mold temperature ($p < 0.0001$, ANOVA) and reached a plateau at ~370°C (Fig. 1(a–c)), although all differences between temperatures greater than 355°C were not statistically significant (Table I). Scaffolds prepared with the LT3UF PEEK powder exhibited a greater compressive modulus ($p < 0.01$, ANOVA), no difference in yield strength ($p = 0.72$, ANOVA), and a lower yield strain ($p < 0.001$, ANOVA) compared to the LT1PF PEEK powder overall, although differences between PEEK powders at a given mold temperature were typically not statistically significant (Fig. 1(a–c)). Scaffolds molded at temperatures greater than 365°C exhibited an initial linear elastic response followed by a yield point and permanent deformation (Fig. 2). Scaffolds molded at temperatures less than 365°C exhibited an initial linear elastic response followed by numerous localized brittle failure events and reloading (Fig. 2). This behavior was visually evident as specimens molded at temperatures greater than 365°C remained intact upon loading beyond the yield point while specimens molded at temperatures less that 365°C produced fragments and debris upon loading beyond the yield point. The ductile–brittle transition qualitatively appeared to occur at a lower mold temperature in scaffolds prepared with the LT1PF PEEK powder compared to the LT3UF PEEK powder.

The crystallinity of both the LT1PF and LT3UF PEEK decreased with increased mold temperature ($p < 0.0001$, ANOVA), although LT3UF may have exhibited a maxima in the range of 360–375°C (Fig. 1(d)). The general trend revealed by differences between mold temperatures was that the PEEK matrix in scaffolds molded at 340–375°C exhibited a crystallinity of 20–30%, whereas scaffolds molded at 380–390°C exhibited a crystallinity of 10–20% (Table I; Fig. 1(d)).
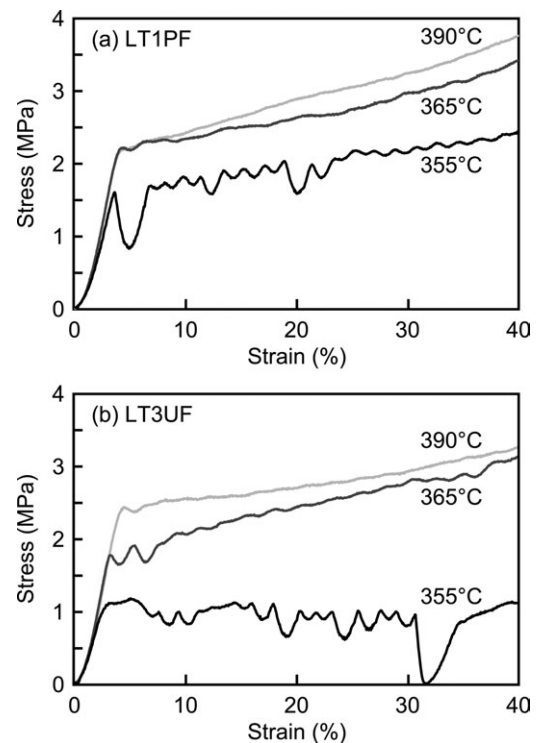
FIGURE 2. Representative stress–strain curves for unconfined uniaxial compression of PEEK scaffolds comprising 75% porosity and 20 vol% HA whisker reinforcement showing the effects of the mold temperature for the (a) LT1PF and (b) LT3UF PEEK powder. The median specimen is shown for each group based on the yield strength. Note that scaffold densification occurred at strains greater than those plotted in this figure.
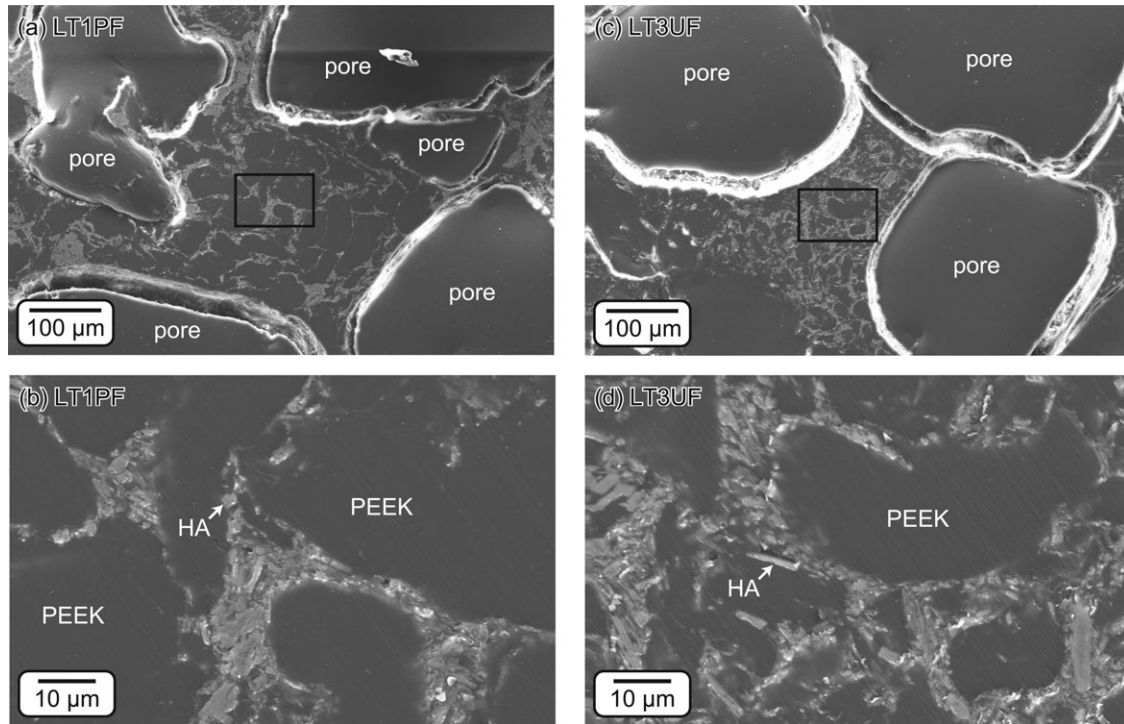
FIGURE 3. Representative SEM micrographs of polished sections showing differences in the microstructure within scaffold struts for scaffolds prepared at a mold temperature of 385°C with the (a and b) LT1PF and (c and d) LT3UF PEEK powder, 75% porosity, and 20 vol% HA whisker reinforcement. Light and dark regions within scaffold struts comprised primarily HA and PEEK, respectively. The region within the box in (a) and (b) is shown at higher magnification in (c) and (d), respectively.

Scaffolds prepared with the LT3UF PEEK powder exhibited a greater crystallinity ($p < 0.0001$, ANOVA) compared with the LT1PF PEEK powder overall, although this difference was consistent and statistically significant only for a given mold temperature of 360–375°C (Fig. 1(d)).

SEM micrographs of polished scaffold sections revealed relatively light and dark regions within scaffold struts (Fig. 3(a,c)). At higher magnification, the light regions were observed to be composed of concentrated HA whiskers segregated between coalesced PEEK particles (Fig. 3(b,d)). Differences in the particle size of the LT1PF and LT3UF PEEK powders were evident by differences in the size of the relatively dark regions (cf. Fig. 3(a,c)). HA reinforcements were observed to be segregated from the PEEK powder regardless of the mold temperature or PEEK powder, but infiltration of the PEEK matrix around the HA whiskers appeared to be greater with increased mold temperature. SEM micrographs of the internal scaffold microstructure on fractured specimens revealed HA whiskers exposed on scaffold strut surfaces (Fig. 4) and a corresponding microtopography, regardless of the mold temperature or PEEK powder.

DISCUSSION

An increased mold temperature resulted in increased compressive mechanical properties, which reached a plateau at ~370°C, but decreased PEEK crystallinity at temperatures greater than 375°C (Fig. 1). Therefore, the minimum mold temperature required to achieve maximum mechanical properties was 370–375°C and this temperature range was concluded to be optimal for compression molding HA whisker-reinforced PEEK scaffolds using either the LT1PF or LT3UF PEEK powder. These results also suggest that the mechanical properties of HA whisker-reinforced PEEK scaffolds were more greatly influenced by densification than the PEEK crystallinity, powder size, or molecular weight, at least within the range of these parameters investigated in this study. Decreased crystallinity is well known to result in decreased stiffness and strength but increased ductility in semicrystalline polymers due to fewer secondary intermolecular bonds and greater disorder. However, at mold temperatures greater than 375°C the PEEK crystallinity decreased without corresponding changes in the mechanical properties.

Densification of polymer powders and composites during compression molding occurs by particle coalescence under elevated temperature and static pressure. HA whisker reinforcements were observed to be segregated between PEEK particles (Fig. 3). Therefore, increased mold temperature resulted in a decreased melt viscosity[30] which facilitated improved infiltration into HA reinforcements segregated at the boundaries between coalescing PEEK particles and improved mechanical properties. Scaffolds molded at temperatures greater 365°C were able to sustain inelastic deformation (Fig. 2) due to sufficient coalescence of PEEK particles despite HA reinforcements acting as a barrier. In contrast, scaffolds molded at temperatures less than 365°C
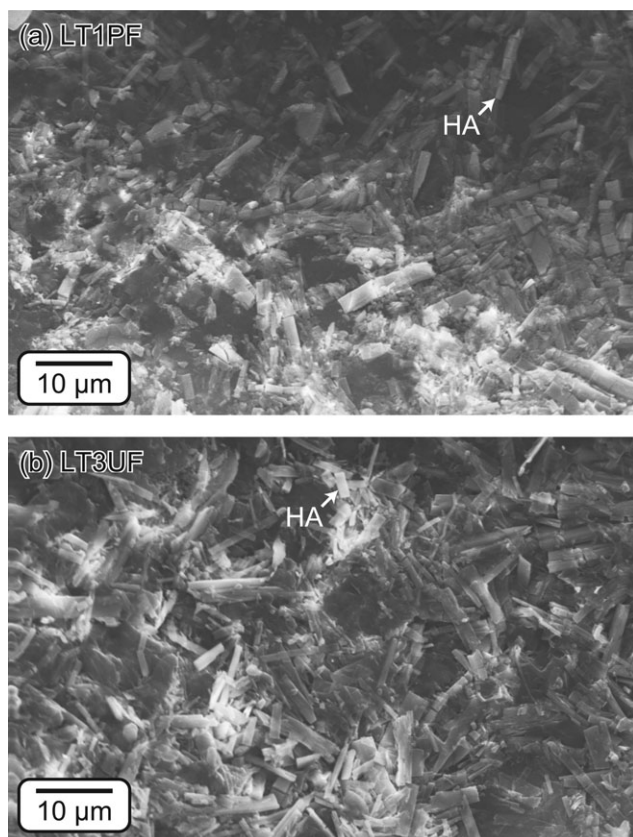
FIGURE 4. Representative SEM micrographs of strut surfaces within scaffolds prepared at a mold temperature of 385°C with the (a) LT1PF and (b) LT3UF PEEK powder, 75% porosity, and 20 vol% HA whisker reinforcement, showing HA whiskers (arrows) exposed on strut surfaces.

exhibited an initial linear elastic response followed by local-ized brittle failure (Fig. 2), most likely at the HA-rich boun-daries between PEEK particles.

These results suggest that further improvement of scaf-fold mechanical properties could be possible by achieving a more uniform dispersion of HA reinforcements within the PEEK matrix through compounding PEEK and HA reinforce-ments before compression molding or inducing flow during molding. HA whiskers were previously observed to be uni-formly distributed within the PEEK matrix, with no evidence of segregation, in dense composites which were compression molded in channel die to induce flow.[14,16,17] Alternatively, chemical coupling agents can improve reinforcement disper-sion and composite mechanical properties,[31] but would cer-tainly be subject to enhanced regulatory scrutiny due to leaching from exposed HA/PEEK interfaces. On the other hand, while possibly detrimental to mechanical properties, the segregation of HA reinforcements between PEEK par-ticles (and porogen particles) ensured that bioactive HA rein-forcements were exposed on scaffold strut surfaces (Fig. 4).

Differences in the size of the LT1PF (~50 μm) and LT3UF (~10 μm) PEEK powders resulted in relatively small or insignificant effects on the scaffold mechanical properties (Fig. 1(a–c)). The slightly greater modulus exhibited by scaffolds prepared with the LT3UF PEEK powder was most likely due to the smaller particle size compared to the LT1PF PEEK powder, which provided increased surface area for improved dispersion of HA reinforcements between coalescing PEEK particles. Considering the preceding discus-sion, the relatively small difference in molecular weight between the LT1PF and LT3UF PEEK powders was not likely to have an appreciable effect.

Decreased crystallinity of the PEEK matrix with increased mold temperature (Fig. 1(d)) was likely due to thermal oxi-dation. Decreased crystallinity with increased temperature was also previously observed for dense HA-reinforced PEEK prepared by injection molding.[23] Thermal oxidation of PEEK and carbon fiber-reinforced PEEK has been observed to become evident at processing temperatures between 380 and 400°C and was attributed to crosslinking via homolytic random chain scission.[32,33] Therefore, mold temperatures greater than 380°C should be approached with caution de-spite mechanical properties that are equal to (and possibly greater than) those at lower mold temperatures (Fig. 1).

Measurements of PEEK crystallinity for the scaffolds in this study were consistent with measurements for dense, unannealed PEEK, and reinforced PEEK.[25] The crystallinity of the PEEK matrix could be increased through an annealing treatment for controlled recrystallization.[25] Furthermore, the potential for oxidation could be further reduced by decreased residence time and the use of an inert gas environment. On the other hand, while detrimental for stiffness and strength, lower crystallinity is known to be beneficial for ductility and toughness,[25,34] and did not influence biocompatibility in vivo.[34] Future studies might consider the effects of PEEK crystallinity and HA reinforcement on the fracture toughness of dense PEEK composites and the impact toughness of PEEK scaffolds.

PEEK crystallinity measurements in this study utilized a 50 μm^2 aperture and therefore represented an average mea-surement for the microstructure within scaffold struts. How-ever, reinforcement phases are known to influence PEEK crystallization.[24] Therefore, the aperture size was reduced to 10 μm^2 for scaffolds molded at 375°C to more closely exam-ine differences in the crystallinity within LT1PF PEEK par-ticles compared to that of the PEEK infiltrating reinforce-ments segregated at the boundaries between coalescing PEEK particles. The crystallinity within PEEK particles was approximately 3% lower ($p < 0.05$, ANOVA) than that within segregated HA reinforcements. This suggests that HA rein-forcements promoted the formation of a more highly crystal-line interphase region possibly similar to that observed with carbon fibers,[24] and further investigation is warranted. This may also explain the greater crystallinity of scaffolds pre-pared with LT3UF compared to LT1PF PEEK, because HA reinforcements were more uniformly distributed within the PEEK powder of greater surface area (Fig. 3).

The apparent compressive modulus, yield strength, and yield strain for HA whisker-reinforced PEEK scaffolds molded at 370–375°C was 75–92 MPa, 2.0–2.2 MPa, and 2.5–3.6%, respectively (Table II). Therefore, these bioactive PEEK scaffolds were able to mimic the compressive modu-lus and yield strength of human vertebral trabecular bone

TABLE II. Comparison of the Compressive Elastic Modulus (E), Yield Strength (YS), and Yield Strain (ε_y) Measured for PEEK Scaffolds Comprising 75% Porosity and 20 vol% HA Whisker Reinforcement Compared with Human Vertebral Trabecular Bone

	Porosity (%)	Apatite Content (vol%)	E (MPa)	YS (MPa)	ε_y (%)
HA whisker-reinforced PEEK scaffolds molded at 370–375°C	75	20	75–92	2.0–2.2	2.5–3.6
Human vertebral trabecular bone[35,36]	~80–95	~40	20–500	0.5–4	0.7–1.0

(Table II). Moreover, the compressive yield strain exceeded that exhibited by human vertebral trabecular bone (Table II). Note that the bioactive PEEK scaffolds in this study achieved these mechanical properties at a lower level of porosity compared to human vertebral trabecular bone; however, scaffolds with 75% porosity are commonly reported to support bone ingrowth.[37,38] Similar scaffolds prepared using identical processing methods were previously reported to exhibit interconnected porosity with a mean pore size in the range 200–300 μm,[21] which is known to be favorable for osteointegration.[37,38] Therefore, HA whisker-reinforced PEEK scaffolds prepared by compression molding and porogen leaching appear to be well suited for biologic fixation of permanent implants adjacent to trabecular bone, such as interbody spinal fusion devices, although further research is needed to investigate bone ingrowth *in vivo*.

CONCLUSIONS

An increased mold temperature resulted in increased compressive modulus, yield strength, and yield strain, reaching a plateau at ~370°C, for compression molded PEEK scaffolds comprising 75% porosity and 20 vol% HA whisker reinforcement (Fig. 1(a–c)). HA reinforcements were observed to be segregated between PEEK particles, which inhibited PEEK particle coalescence during compression molding at temperatures <365°C (Figs. 2 and 3) but also ensured that bioactive HA reinforcements were exposed on scaffold strut surfaces (Fig. 4). An increased mold temperature also resulted in decreased PEEK crystallinity, particularly for scaffolds prepared at temperatures greater than 375°C (Fig. 1(d)). The PEEK powder exhibited relatively minor effects on the scaffold mechanical properties and crystallinity. Therefore, the results of this study suggested an optimum mold temperature of 370–375°C for HA whisker-reinforced PEEK scaffolds prepared by compression molding and porogen leaching with either the LT1PF or LT3UF PEEK powder. The apparent compressive modulus, yield strength, and yield strain for scaffolds molded at 370–375°C was 75–92 MPa, 2.0–2.2 MPa, and 2.5–3.6%, respectively, which was within the range of mechanical properties exhibited by human vertebral trabecular bone (Table II).

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