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Research paper

Effects of the reinforcement morphology on the fatigue properties of hydroxyapatite reinforced polymers

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ABSTRACT

The objective of this study was to examine the effects of the hydroxyapatite (HA) reinforcement morphology and content on the fatigue behavior of HA reinforced high density polyethylene (HDPE). To this end, HDPE was reinforced with 20 and 40 vol% of either HA whiskers or an equiaxed HA powder, and tested in four-point bending fatigue under simulated physiological conditions. The fatigue life, mechanical property degradation and failure surfaces were compared between experimental groups. HDPE reinforced with HA whiskers exhibited a four- to five-fold increase ($p < 0.001$, T-test) in fatigue life compared to an equiaxed powder for either the 20 and 40 vol% reinforcement level. Composites containing 40 vol% HA exhibited decreased fatigue life compared to those with 20 vol% HA for either reinforcement morphology ($p < 0.0001$, ANOVA). HA whisker reinforced HDPE exhibited less stiffness loss, permanent deformation (creep) and energy dissipation at a given number of cycles compared to HA powder. Thus, HA whisker reinforced HDPE was more tolerant of fatigue damage due to either microcracking or polymer plasticity. Scanning electron microscopy of failure surfaces and surface microcracks showed evidence of toughening by uncracked ligaments, crack tip plasticity, polymer fibril bridging and HA whisker pullout. The results of this study suggest that the use of HA whiskers, in place of HA powder, is a straightforward means to improve the fatigue life and damage tolerance of HA reinforced polymers for synthetic bone substitutes.

1. Introduction

A variety of hydroxyapatite (HA) reinforced polymers are under investigation for use in a variety of orthopedic applications, including synthetic bone graft substitutes, implant fixation, and bone ingrowth or tissue engineering scaffolds (Roeder et al., 2008; Rezwan et al., 2006). The motivation is that currently available synthetic biomaterials do not adequately provide both the biological and mechanical properties required. In principle, the composition and organization of phases in a composite material may be tailored to mimic the properties of natural tissue as closely as possible. The extracellular matrix (ECM) of bone tissue is itself a two-phase composite of a predominately type-I collagen matrix reinforced with apatite crystals (Rho et al., 1998).

HA reinforced polymers were pioneered by Bonfield et al. (1981), with the study of HA reinforced high density polyethylene (HDPE) (Bonner et al., 2002; Di Silvio et al.,

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2002; Wang et al., 1998). HDPE containing 40 vol% HA was commercialized under the trade name HAPEX^{TM} for use in non-load-bearing otologic and maxillofacial implants (Wang et al., 1998). However, use of HAPEX^{TM} in load-bearing applications was limited in part due to the low stiffness and strength of HDPE. Consequently, a variety of non-degradable polymers have been investigated, including polyetheretherketone (PEEK) (Abu Bakar et al., 2003), polymethylmethacrylate (PMMA) (Harper et al., 1995), ultra-high molecular weight polyethylene (UHMWPE) (Fang et al., 2006) and polypropylene (PP) (Bonner et al., 2001), among others. While static tensile, compressive or flexural properties, such as the elastic modulus and ultimate strength, are often reported for these materials, relatively few studies have examined fatigue.

The fatigue properties of HAPEX^{TM} were examined under fully reversed uniaxial tension–compression and torsion, as well as biaxial tension–compression and torsion, for varying levels of applied stress (Ton That et al., 2000a,b). Hydrostatically extruded HAPEX^{TM} exhibited anisotropic mechanical properties and a significantly improved flexural fatigue life compared to conventional, isotropic HAPEX^{TM}, due to molecular alignment (McGregor et al., 2000). HA reinforced PEEK was tested in tension–tension fatigue at various levels of stress and HA content, showing the detrimental effects of increased HA content on the fatigue life (Abu Bakar et al., 2003; Tang et al., 2004). The effect of the reinforcement morphology on the fatigue behavior of HA reinforced polymers has not been investigated.

All the HA reinforced polymers described above used HA powders with an approximately equiaxed morphology. Therefore, these composites exhibited isotropic mechanical properties which, with the exception of HA reinforced PEEK, typically fell short of the elastic modulus and ultimate strength of human cortical bone tissue (Roeder et al., 2008). In contrast, apatite crystals in the ECM of bone are elongated (plate-like) and preferentially oriented in directions of principal stress (Rho et al., 1998; Wenk and Heidelbach, 1999). Therefore, HA whiskers have been investigated as a reinforcement phase in polymers.

HA whisker reinforced polymer composites have exhibited improved mechanical properties compared to the use of an equiaxed powder (Roeder et al., 2003). Whiskers may be preferentially oriented along one specimen direction during processing, mimicking the composition, morphology and preferred orientation of apatite reinforcements in bone tissue. HA whisker reinforced HDPE and PEEK were prepared with a preferred orientation of HA whiskers resulting in anisotropic mechanical properties similar to cortical bone tissue (Converse et al., 2007; Roeder et al., 2003; Yue and Roeder, 2006). However, the effect of HA whiskers on fatigue properties has not been investigated.

Therefore, the objective of this study was to examine the effects of the HA reinforcement morphology and content on the fatigue behavior of HA reinforced HDPE. To this end, HDPE was reinforced with 20 and 40 vol% of either HA whiskers or an equiaxed HA powder and tested in four-point bending fatigue under simulated physiological conditions. The reinforcement levels were selected to compare composites with a bone-mimetic reinforcement level (40 vol%) versus composites at a lower reinforcement level (20 vol%) exhibiting a ~40% greater tensile strength and ~50% lower elastic modulus (Roeder et al., 2003). The fatigue life, mechanical property degradation and failure surfaces were compared between experimental groups.

2. Materials and methods

2.1. *Starting materials*

Commercially available high density polyethylene (HDPE) pellets (Product #42797-7, Sigma-Aldrich, Milwaukee, WI) were reduced to a fine powder via a batch precipitation process. 20 g HDPE pellets were added to 1600 ml *p*-zylene, heated to boiling and refluxed for 10 min at ~137 °C until the HDPE pellets were completely dissolved. The solution was allowed to cool under rapid stirring, resulting in precipitation of fine HDPE particles. After reaching room temperature, the HDPE particles were collected via vacuum filtration, washed in ethanol, and dried at 90 °C for 2–4 h. The HDPE particles were observed to be spherical and 5–50 μm in diameter (Roeder et al., 2003).

HA whiskers were precipitated by a hydrothermal reaction using the chelate decomposition method. The morphology of the whiskers can be controlled by adjusting the heating rate, stirring rate and chelating acid, among other variables (Roeder et al., 2006). The synthesis conditions and characterization of the whiskers used in this study were described in detail elsewhere, resulting in a mean length and aspect ratio (± standard deviation) of 18 ± 8.9 μm and 7.9 ± 3.4, respectively (Roeder et al., 2003).

An equiaxed HA powder was obtained commercially (Product #21221, Fluka Chemical Co., Buchs, Switzerland). The as-received powder was ground using a mortar and pestle to minimize agglomerates, and the powder was stored at 90 °C to remove residual moisture. The mean diameter of this powder was reported previously as 1.3 ± 0.4 μm, which was comparable to the width of the whiskers (Roeder et al., 2003).

2.2. *Composite processing*

HA reinforced HDPE composites were prepared using a powder mixing and compression molding method previously described in detail (Roeder et al., 2003). Briefly, the required amounts of HDPE powder and HA whiskers or powder were added to ethanol under stirring and sonication for 10 min. The particle suspension was quickly vacuum filtered to avoid phase separation and dried at 90 °C for 1–2 h. The dry composite powder mixture was placed into a pellet die and densified at 5 MPa to form a composite preform. The dense composite perform was compression molded in an open channel die heated to 145 °C. During molding, the viscous polymer was extruded from the center of the die, where the preform was placed, toward each end, and shear forces acted to preferentially orient the HA whiskers along the long axis of the molded composite bar. Subsequent texture analysis using x-ray diffraction (XRD) has been used to confirm and characterize the preferred crystallographic and morphological orientation of HA whiskers along the long

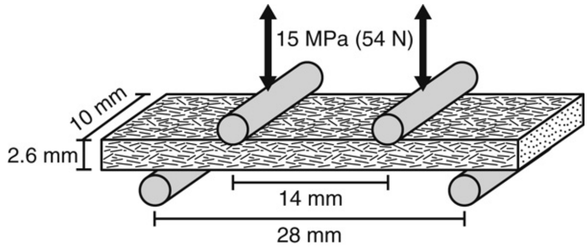

Fig. 1 – Schematic diagram showing the specimen dimensions and loading configuration. The preferred orientation of HA whiskers relative to the specimen orientation is shown on the specimen surface (not to scale).

axis of the composite bar (Yue and Roeder, 2006). As-molded composite beams measured approximately 120 mm in length, 10 mm in width and 2.6 mm in thickness, and were sectioned into 35 mm length segments for fatigue testing. Specimen edges were polished with 400, 800 and 1200 grit SiC paper to remove minor surface defects.

2.3. *Fatigue testing*

Fatigue testing was carried out under conditions designed to replicate ASTM D790 specimen dimensions (ASTM, 1997) and physiological conditions. Specimens were placed in phosphate buffered saline for at least 24 h prior to testing. Specimens were loaded in four-point bending with 28 and 14 mm major and minor spans, respectively (Fig. 1). Load was applied in a sinusoidal waveform to a maximum tensile stress of 15 MPa and a minimum stress of 1.5 MPa ($R = 0.1$) at a frequency of 2 Hz until failure using an electromagnetic test instrument (ELF-3300, ElectroForce systems group of Bose Corp., Eden Prairie, MN). All tests were conducted in phosphate buffered saline at 37 ± 0.5 °C.

Experimental groups included HDPE reinforced with 20 and 40 vol% of either HA whiskers or powder. Five specimens were prepared and tested for each group. The fatigue life was measured as the total number of loading cycles at failure. One-way analysis of variance (ANOVA) (JMP 5.1, SAS Institute, Inc., Cary, NC) was used to compare 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 also used to examine the effects and interaction of the reinforcement morphology and content on the fatigue life.

Load–deflection data was collected for a full loading cycle every 100 cycles at a sampling rate of 600 data points per cycle. Beam deflections were measured using a linear variable displacement transducer (LVDT). From this data, the beam stiffness, permanent deformation and energy dissipation was determined as a function of the number of loading cycles. The secant stiffness was measured from the loading portion of the load–deflection curve (Fig. 2). The unloading stiffness was measured from a linear fit of the upper 20% of the unloading portion of the load–deflection curve, offset 5% from the maximum load (Fig. 2). The normalized stiffness, which is equivalent to a normalized elastic modulus, was determined as the ratio of the stiffness at a given number of loading cycles by the initial beam stiffness, taken as the average of the first 10 loading cycles. Permanent deformation (creep) was measured as the minimum deflection of the hysteresis loop for each loading cycle (Fig. 2). Lastly, the energy dissipated per cycle was measured by the area inside each hysteresis loop via numerical integration using Simpson's rule.

Failure surfaces for specimens exhibiting the median fatigue life in each experimental group were imaged using scanning electron microscopy (SEM) (Evo 50, LEO Microscopy Ltd, Cambridge, U.K.) with an accelerating voltage of 13 kV and a working distance of 7–10 mm. Additionally, a specimen reinforced with 20 vol% HA whiskers was loaded to 500,000 cycles, which was approximately two-thirds of the expected fatigue life. The lower beam surface, where maximum tensile stresses occurred, was also imaged using SEM. All SEM specimen surfaces were coated with gold–palladium using sputter deposition.

3. Results

HDPE reinforced with HA whiskers exhibited a four- to five-fold increase ($p < 0.001$, T-test) in fatigue life compared to an equiaxed powder for either the 20 or 40 vol% reinforcement

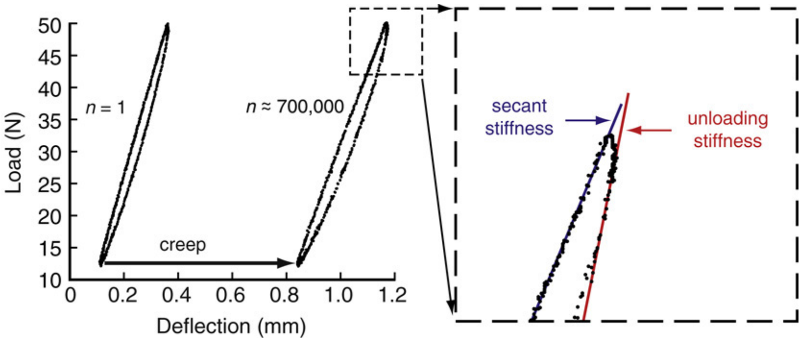

Fig. 2 – Exemplary load–deflection hysteresis loops for the initial and final loading cycles of a specimen reinforced with 20 vol% HA whiskers. At low cycles, the secant loading stiffness was nearly identical to a linear fit of the unloading stiffness. At high cycles, the unloading stiffness deviated from the secant loading stiffness, as shown on the right. Permanent deformation (creep) was measured by translation of the hysteresis loops.

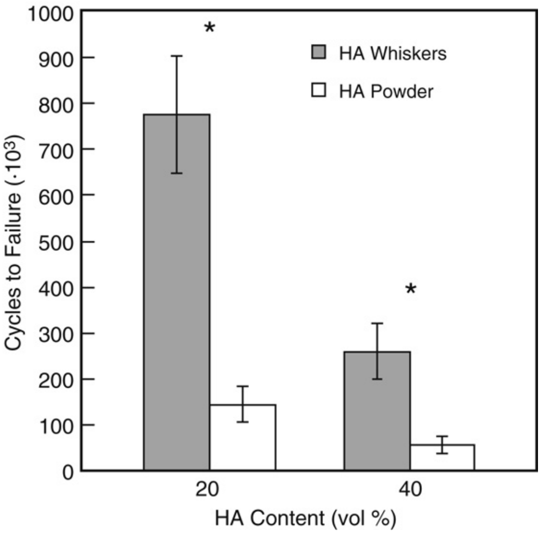

Fig. 3 – Mean fatigue life (number of cycles to failure) for HDPE reinforced with 20 and 40 vol% HA whiskers or powder. Error bars span one standard deviation. Asterisks denote a statistically significant difference in fatigue life between HA whiskers and powder at a given HA content ($p < 0.001$, T-test). Two-way ANOVA showed that the HA morphology and content each had a statistically significant effect on the fatigue life, and a statistically significant interaction ($p < 0.0001$).

level (Fig. 3). Composites containing 40 vol% HA exhibited decreased fatigue life compared to those with 20 vol% HA for either reinforcement morphology. Moreover, the HA morphology and content each had a statistically significant effect on the fatigue life, and a statistically significant interaction ($p < 0.0001$, ANOVA).

Load–deflection curves for all composites were initially nearly linearly elastic during both loading and unloading. The secant stiffness of the loading curve and a linear fit of the unloading stiffness were nearly identical throughout most of the fatigue life, until the last ~1000 cycles prior to failure (Fig. 2). The unloading stiffness exhibited less variability and, unlike the secant stiffness, would not be expected to be influenced by plasticity. Therefore, the unloading stiffness was used to determine the normalized beam stiffness.

HA whisker reinforced specimens exhibited less stiffness loss at a given number of cycles compared to HA powder at the 40 vol% level (Fig. 4(b)), but not at the 20 vol% level (Fig. 4(a)). HDPE reinforced with 20 vol% HA whiskers or powder exhibited a long plateau of a relatively constant stiffness, followed by rapid stiffness degradation immediately prior to failure at greater than 100,000 cycles (Fig. 4(a)). In contrast, HDPE reinforced with 40 vol% HA exhibited a continuous and nearly linear reduction in stiffness over most of the fatigue life beginning at 1000–10,000 cycles (Fig. 4(b)).

HA whisker reinforced specimens at either volume fraction exhibited less permanent deflection (creep) at a given number of loading cycles compared to HA powder (Fig. 5). HDPE reinforced with 20 vol% HA whiskers or powder exhibited a gradual increase in permanent deflection followed by a rapid increase immediately prior to failure (Fig. 5(a)). HDPE reinforced with 40 vol% HA exhibited a continuous and nearly linear increase in permanent deflection until failure (Fig. 5(b)).

HA whisker reinforced specimens exhibited a lower rate of energy dissipation at a given number of cycles compared to HA powder (Fig. 6). HDPE reinforced with 20 vol% HA whiskers or powder exhibited a relatively constant level of energy dissipation throughout most of the fatigue life, followed by a sudden increase immediately prior to failure (Fig. 6(a)). In contrast, HDPE reinforced with 40 vol% HA exhibited a continuous and nearly linear increase in the energy dissipated per loading cycle over most of the fatigue life beginning between 1000 and 10,000 cycles (Fig. 6(b)).

SEM micrographs showed the presence of HA whisker or powder reinforcements on each failure surface and HDPE fibrils extending away from the failure surface (Fig. 7). HDPE fibrils were longer, and the failure surface was more tortuous, for composites reinforced with HA whiskers compared to powder. Fatigue cracks and microcracks were observed on the tensile surface of a specimen reinforced with 20 vol% HA whiskers loaded to two-thirds of its expected fatigue life (Fig. 8). All cracks were generally oriented perpendicular to

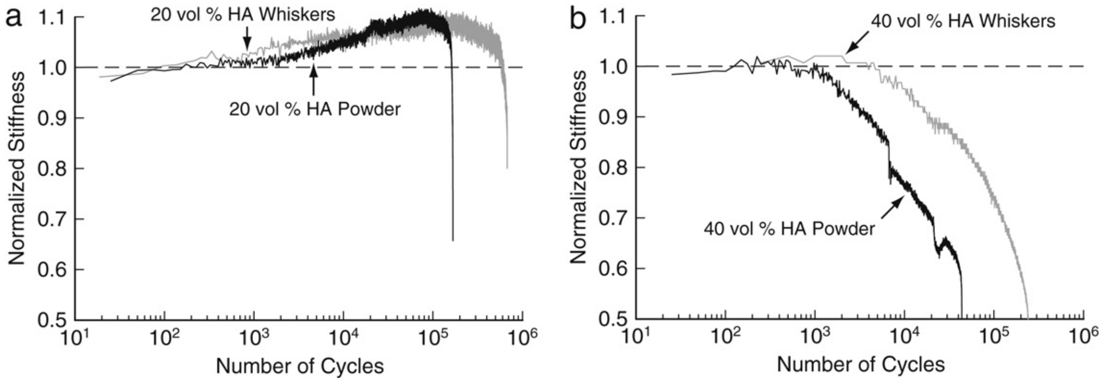

Fig. 4 – Normalized stiffness loss from a linear fit of the unloading portion of the load–deflection curve for HDPE reinforced with (a) 20 and (b) 40 vol% HA whiskers or powder. Data is plotted for specimens that exhibited the median fatigue life in each group.

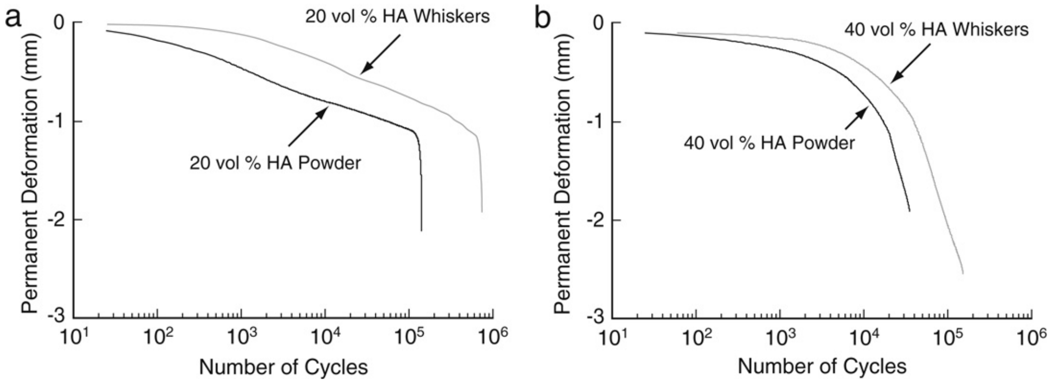

Fig. 5 – Permanent deformation (creep) for HDPE reinforced with (a) 20 and (b) 40 vol% HA whiskers or powder. Data is plotted for specimens that exhibited the median fatigue life in each group.

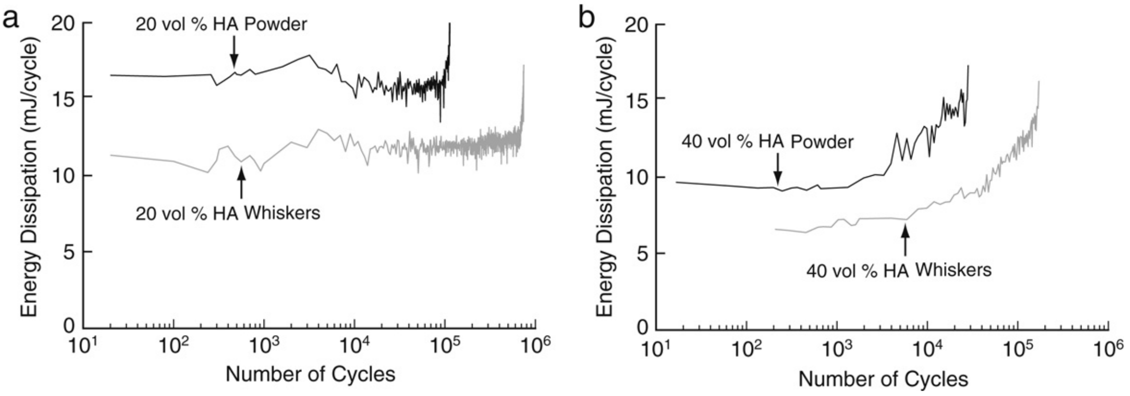

Fig. 6 – Energy dissipated per loading cycle for HDPE reinforced with (a) 20 and (b) 40 vol% HA whiskers or powder. Data is plotted for specimens that exhibited the median fatigue life in each group.

the direction of maximum tensile stress, propagating toward the center from the specimen edges. Both the failure surfaces and surface cracks showed evidence of toughening by uncracked ligaments (Fig. 8(a)), crack tip plasticity (Fig. 8(b)), polymer fibril bridging (Figs. 7 and 8(b) and (c)) and HA whisker pullout (Figs. 7(b), (d) and 8(b)).

4. Discussion

HA whiskers significantly increased the fatigue life, by four- to five-fold, compared to an equiaxed HA powder (Fig. 3). This result was expected due to improved load transfer along the length of HA whiskers and increased resistance to crack propagation (Fig. 8). These results suggest that the use of HA whiskers, in place of HA powder, to reinforce other polymers will result in similar improvements in fatigue life. Thus, HA whisker reinforcements provide a straightforward means to improve the fatigue life of HA reinforced polymers for synthetic bone substitutes.

Fatigue damage occurred as a combination of microcracks and polymer plasticity (Fig. 8). Microcracking was reflected by changes in the elastic properties measured by the unloading stiffness (Fig. 4). Polymer plasticity was reflected by the measured permanent deflection (creep) (Fig. 5) and was manifested as microvoids between polymer fibrils (Figs. 7 and 8). Plastic deformation of the polymer preceded the formation of microcracks (Figs. 4 and 5) and was likely responsible for the initial increase in stiffness for HDPE reinforced with 20 vol% HA (Fig. 4(a)). The normalized stiffness for HDPE reinforced with 20 vol% HA, but not 40 vol% HA, increased by as much as 10% prior to failure. This effect was also reported for HAPEX$^{\text{TM}}$, and was suggested to be the result of polymer macromolecules aligning during plastic deformation (McGregor et al., 2000; Ton That et al., 2000a). The absence of this behavior in HDPE reinforced with 40 vol% HA was likely due to a lower resistance to crack initiation and propagation as the composites become more brittle at higher volume fractions of HA. In other words, deformations large enough to induce macromolecule alignment and stiffening were preceded by fatigue crack propagation and failure. Finally, energy dissipation reflected the rate of damage accumulation for all processes, including polymer plasticity, microcrack initiation and fatigue crack propagation (Fig. 6).

Under the conditions of this study, mechanical property degradation during fatigue was more strongly influenced by

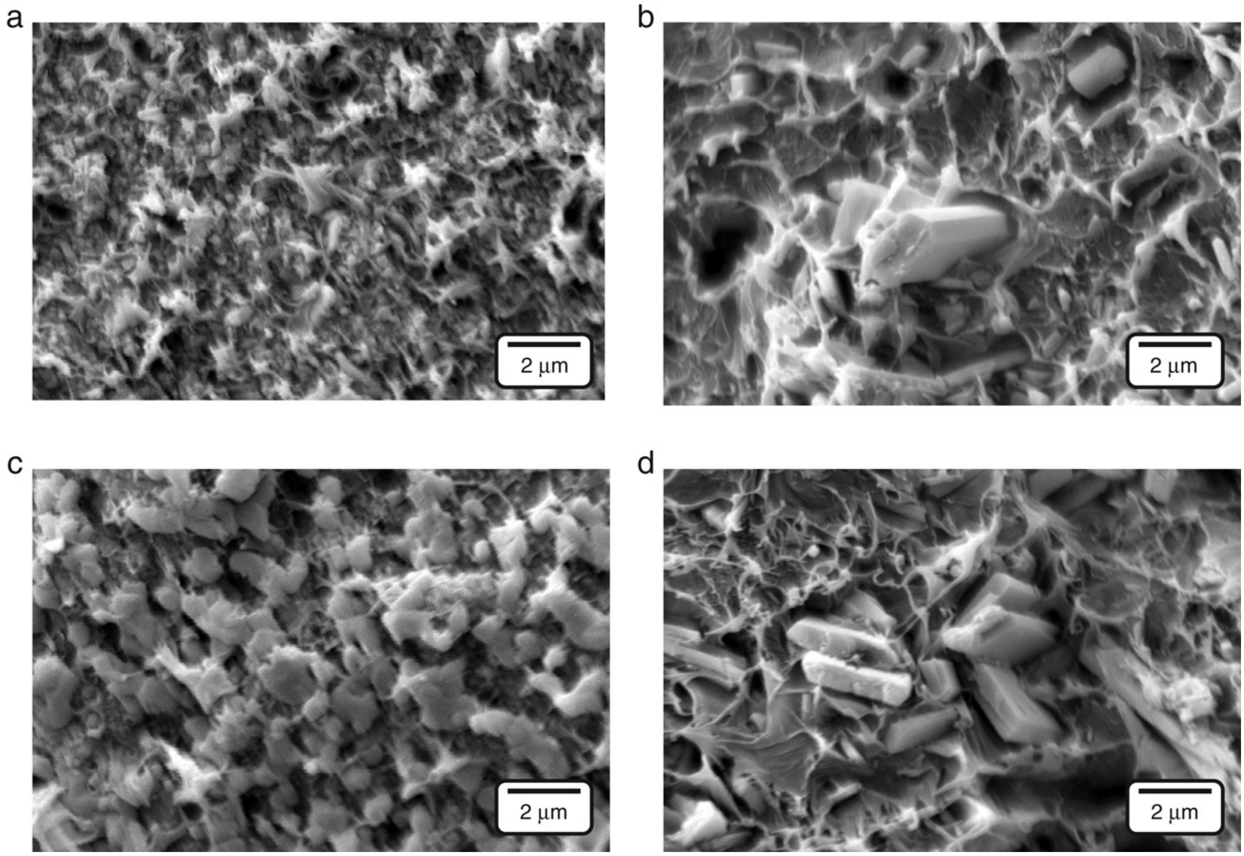

Fig. 7 – SEM micrographs of failure surfaces for specimens that exhibited the median fatigue life in each group: (a) 20 vol% HA powder, (b) 20 vol% HA whiskers, (c) 40 vol% HA powder and (d) 40 vol% HA whiskers.

the reinforcement volume fraction than the reinforcement morphology (Figs. 4–6). Similar degradation behavior was observed at similar reinforcement levels, regardless of the HA reinforcement morphology, and different behavior was observed between reinforcement levels for the same HA morphology. This suggests that at lower reinforcement levels (20 vol%) property degradation was governed by the ductile polymer matrix, whereas behavior at higher reinforcement levels (40 vol%) was governed by the reinforcement phase and interface. Note, however, that the HA whisker length is known to degrade during processing resulting in a decrease of the mean aspect ratio to approximately four after molding (Yue and Roeder, 2006). Therefore, the stronger effect of the reinforcement level is not surprising and the four- to five-fold increase in fatigue life for only a four-fold increase in aspect ratio (from powder to whisker) is all the more encouraging.

On the other hand, significant creep occurred prior to failure in all experimental groups (Fig. 5). The plastic deformation reached over ten times the elastic deformation produced by a physiological stress. This behavior was primarily due to the high ductility of HDPE and could be detrimental to long term use in load-bearing applications. The use of other polymers with higher strength, such as PEEK, is expected to alleviate this limitation. A similar fatigue study for HA whisker reinforced PEEK is currently in progress.

Observations of failure surfaces using SEM suggested that composites failed primarily by interfacial debonding (Ton That et al., 2000a), and, in the case of HA whisker reinforced HDPE, whisker pullout. The longer HDPE fibrils observed for HA whisker reinforced HDPE suggest a slower rate of crack growth compared to HA powder reinforced HDPE, where a less tortuous failure surface suggests a higher rate of crack growth. This also suggests that HA whiskers, which were aligned normal to the crack plane, enhanced the extent of polymer fibril bridging along the crack. Additionally, longer HDPE fibrils were observed on composites reinforced with 20 vol% HA compared to 40 vol% HA for either whisker or powder reinforcements, though less pronounced for whiskers (Fig. 7). Combined with the measurements of mechanical property degradation discussed above, these observations suggest that crack initiation was governed primarily by reinforcement level, while crack propagation was governed primarily by the reinforcement morphology.

Interestingly, observations of fatigue cracks and microcracks on the tensile surface (Fig. 8) were similar to those observed on cortical bone beams loaded in bending fatigue (Kruzic et al., 2006) and during fracture toughness tests (Ager et al., 2006). Bridging was observed in the form of uncracked ligaments of the composite material itself (Fig. 8(a)), as well as polymer fibrils (Figs. 7 and 8(b) and (c)). Crack tip plasticity (Fig. 8(b)) and HA whisker pullout (Figs. 7(b), (d) and 8(b)) were also observed. Since, unlike bone, these composites have no structural features larger than the HA whiskers, the origin of

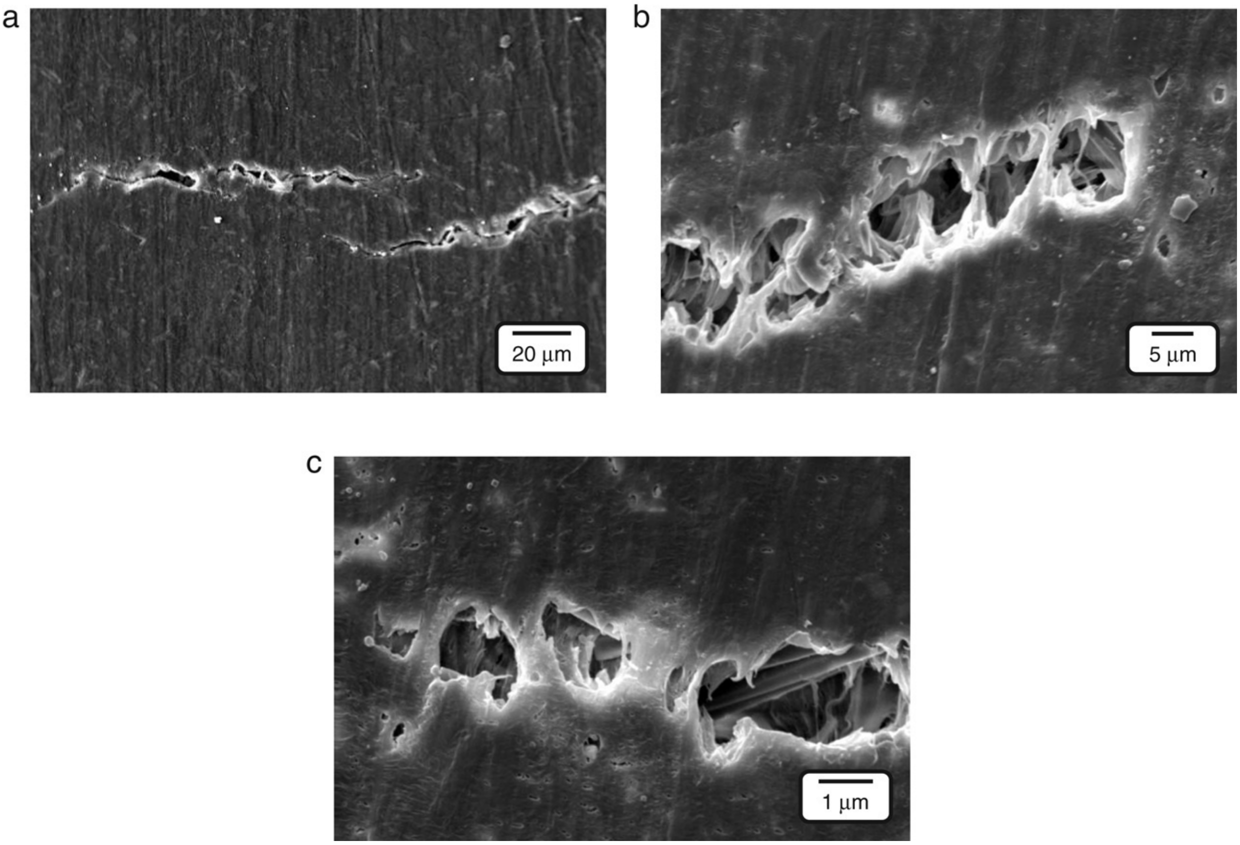

Fig. 8 – SEM micrographs showing fatigue cracks and microcracks on the tensile surface of a specimen reinforced with 20 vol% HA whiskers, which was loaded to approximately two-thirds of the expected fatigue life: (a) an uncracked ligament bridging a fatigue crack; (b) crack tip plasticity, polymer fibril bridging and HA whisker pullout at a crack tip; and (c) polymer fibril bridging. Note that all micrographs are oriented such that the applied tensile stress is vertical, normal to the direction of crack propagation.

the uncracked ligaments was unclear. Overall, noting the effects of the HA reinforcement level on the fatigue life, crack tip plasticity (or blunting) and bridging due to the polymer fibrils appeared to be the dominant toughening mechanisms.

5. Conclusions

HDPE reinforced with HA whiskers exhibited a four- to five-fold increase in fatigue life compared to an equiaxed powder for either the 20 and 40 vol% reinforcement level. Composites containing 40 vol% HA exhibited decreased fatigue life compared to those with 20 vol% HA for either reinforcement morphology. HA whisker reinforced HDPE exhibited less stiffness loss, permanent deformation (creep) and energy dissipation at a given number of cycles compared to HA powder. Therefore, HA whisker reinforced HDPE was more tolerant of fatigue damage due to either microcracking or polymer plasticity. Failure surfaces and surface cracks showed evidence of toughening by uncracked ligaments, crack tip plasticity, polymer fibril bridging and HA whisker pullout. The results of this study suggest that the use of HA whiskers, in place of HA powder, is a straightforward means to improve the fatigue life and damage tolerance of HA reinforced polymers for synthetic bone substitutes.

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