Fracture Mechanism of Bioceramic Beads Filled Biopolymer Composite Material

J. J. Duckworth[1], M. Todo[2*]

[1]Interdisiplinary Graduate School of Engineering Sciences, Kyushu University, Fukuoka, Japan
[2]Research Institute for Applied Mechanics, Kyushu University, Fukuoka, Japan

*Corresponding author: todo@riam.kyushu-u.ac.jp

1. Introduction

This investigation fabricated and then characterized micrometer scale beads of hydroxyapatite (HA), then combined them in a poly L-lactic acid (PLLA) matrix to form a composite biomaterial. This material is hoped to combine the high strength and fracture toughness of PLLA with the biointegrating properties of HA for use in bone plate implants [1]. Mechanical testing showed that the beads reduced the fracture toughness of pure PLLA, and the mechanism for this decrease was investigated. 3-point notched bending tests, electron probe micro-analysis (EPMA), optical microscopy and scanning electron microscopy (SEM) were all used to investigate the fracture behaviour of the beaded PLLA material and explain the observed behaviour.

2. Methods

A two-step process was used to produce HA beads [2]. Firstly, α-tricalcium phosphate (α-TCP) powder and 1% sodium alginate solution were blended and subjected to ultrasonic dispersion to create a smooth slurry, then dripped into a 4°C 1% calcium chloride solution through a 30G gauge needle to produce beads of fixed radius. The preliminary beads of α-TCP confined in the crosslinked calcium alginate were dried at room temperature, before firing at 1300°C for 5 hours to produce the final HA beads. X-ray diffraction and SEM showed the beads to in fact be semi-porous biphasic calcium phosphates, a mixture of α-TCP and HA, with a mean bead radius of 750±50 µm.

Inclusion into the PLLA matrix was done using a brass mold, square grid and hot press. After hot pressing the material was cut to shape, then notched using a 1mm diamond tipped saw and razor blade, as outlined in the industry standard, to produce a sharp crack tip, shown in Fig. 1 [3]. Materials with varying concentrations of beads were used, from 0% to 10% by volume.

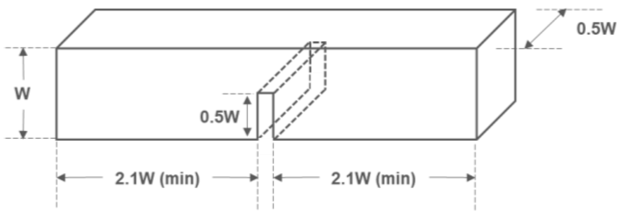

Fig 1. Geometry of single edge notched bending test specimen, from ASTM-399.

Three-point bending tests were used to determine elastic modulus for each material group.

Three-point notched bending tests were used to calculate the critical stress intensity factor, K_{IC}, for each group, using the method outlined in ASTM E399. Fracture surfaces were analyzed using optical and SEM microscopy to locate the types of fracture which may have occurred in each area, and where and how the energy was dissipated during crack propagation.

EPMA was used to track the concentration of calcium across the bead/polymer interface, as a measure of polymer inclusion into the semi-porous beads.

3. Results and discussion

Firstly, the material was successfully fabricated. The beads showed good distributions in the x,y and z axes, and seemed to be well incorporated into the matrix. Figure 2 shows the surface under an optical microscope at 2 times magnification.

Elastic modulus was found to be invariant within error across all bead-containing groups, and only showed a slight increase compared with blank PLLA, from 690±70 MPa to 550±30 MPa on average, indicating that the strain energy was transferring primarily through the polymer matrix.

K_{IC} however, was seen to decrease linearly with bead concentration as shown in Fig 3a. This indicated that the beads were causing a fracture mechanism by means other than stiffening the entire material, whilst still causing a more brittle fracture, indicated by the sharp angle of the load/displacement curve in Fig 3b.

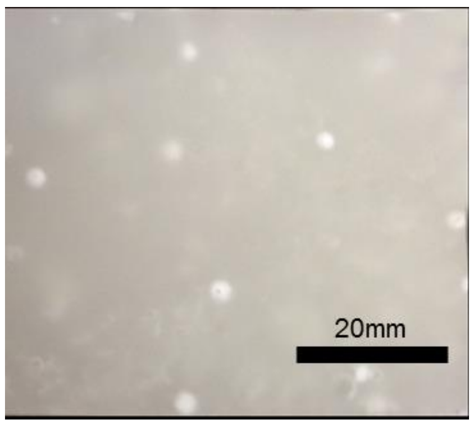

Fig 2. HA beads evenly distributed in PLLA matrix after fabrication.

Imaging showed that the bead polymer interface was not separating and creating voids for crack growth and propagation as might be expected, but instead consistent shearing of the beads along the crack plane were observed, shown in Fig 4a. This indicated polymer intrusion into the beads, confirmed by EPMA, shown in Fig 4b. It also suggested another mechanism is responsible.

It was noted that blank PLLA fracture surfaces showed uniform hackle patterns across all scales, indicating ductile deformation before fracture [4]. Beaded samples however only showed this behaviour in a region below the bead. The region above the bead showed instead a sharp fracture plane, indicating fast, brittle fracture in this region, shown in Fig 5. The limit of this region was a distinct slope away from the middle of the bead, towards a plane at the base of the bead. It is therefore suggested that the bead localizes a region of high stiffness in the surrounding polymer, allowing strain energy density to increase locally.

Upon fracture initiation, this energy is quickly released through the stiffened region to form a brittle fracture, which transitions to a ductile fracture away from the bead.

4. Conclusions

The discovery of this fracture mechanic suggests several ways to improve the fracture toughness of the material further, to make it better suited for bone plate applications, such as; increasing bead porosity, decreasing bead stiffness, decreasing the local stiffness around the bead by altering the polymer bead interaction, increasing the radius of the bead to better integrate with the polymer and reduce local stress concentrations.

It is also necessary to test the material for cell affinity and biocompatibility, to see how osteoclasts will react to the new material surface. Most importantly, these results indicate that it is feasible to create a material with fracture toughness comparable to blank PLLA, but with the increased biocompatibility of HA, and also give us directed avenues of approach for achieving this.

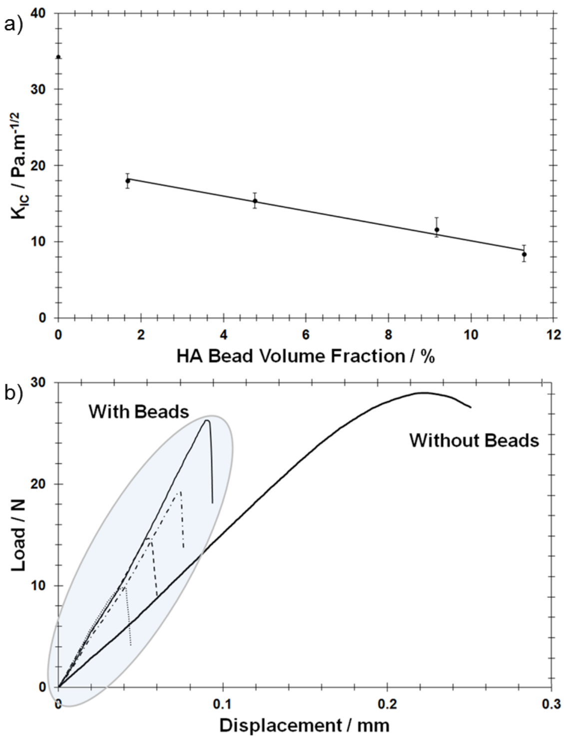

Fig 3. a) K_{IC} of material with bead conc. b) Sample load/displacement curves of each group.

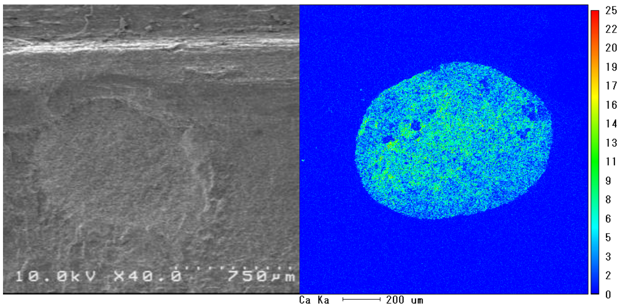

Fig 4. a) SEM image of bead along crack plane b) EPMA Ca conc. of bead at fracture surface.

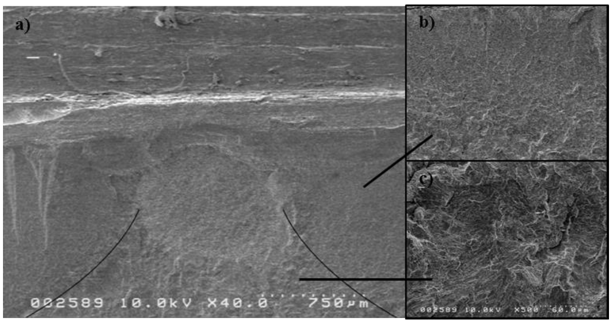

Fig 5. a) SEM image of two regions of fracture surface, b) upper brittle, c) lower ductile fracture.

5. References

[1] S. B. Sulaiman *et al.*, TCP-HA bone scaffold as potential candidate for the formation of tissue engineered bone *Indian J Med Res.*, 137 (6) (2013) 1093–1101.
[2] M. Vallet-Regi, L. M. Rodriguez-Lorenzo and A. J. Salinas, Synthesis and characterization of calcium deficient apatite, *Solid State Ionics*, 101 (1997) 1279-1285.
[3] ASTM E399-17, Standard test method for linear-elastic plane-strain fracture toughness *ASTM International* (2017).
[4] M. Todo, S. D. Park, T. Takayama and K. Arakawa, Fracture mechanics of bioabsorbable PLLA/PCL polymer blends, *Eng Fract Mech.* 74 (12) (2007) 1872-1883.