Effect of filler type on the mechanical properties of self-reinforced polylactide–calcium phosphate composites

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Bioabsorbable polymers are of interest as internal fracture fixation devices. Self-reinforcement has been developed to improve the mechanical properties of the material and the addition of calcium phosphate fillers improves the bioactivity. Composite plates, produced by compression molding preimpregnated sheets of polylactide fibers coated in a polylactide matrix have been degraded in simulated body fluid for up to 12 weeks. Some samples also contained hydroxyapatite or tricalcium phosphate filler particles. Degradation was measured by monitoring the water uptake and mass decrease of the samples, as well as carrying out four point bend tests to assess the mechanical properties of the material. By 12 weeks, it was found that the unfilled samples absorbed more water and showed greater mass loss than the samples containing calcium phosphate fillers. Also, the flexural modulus and yield stress decreased significantly at week 12 for the unfilled samples. Adding hydroxyapatite (HA) or tricalcium phosphate (TCP) to the composite increased the flexural modulus and yield strength to values within the range of those reported for cortical bone and these values were maintained over the 12-week period.

1. Introduction

Bioabsorbable devices for internal fracture fixation have been in clinical use since the 1980s [1] and have advantages over conventional materials such as stainless steel [2]. Degradable polymers such as polylactide show a gradual reduction in mechanical properties as they degrade, allowing loads to be progressively transferred to the bone, so reducing stress shielding. Since the implant is ultimately totally resorbed, a secondary removal operation is not required and risks of long-term complications due to metallic implants are reduced. However, the major drawback of using non-reinforced resorbable polymers is that they have insufficient strength and stiffness for use in load bearing applications [3].

One way in which the mechanical properties have been successfully improved is to self-reinforce the polymer with fibers of the same chemical composition as the matrix [4–6]. The mechanical properties are greatly improved by the addition of highly orientated unidirectional fibers. Other attempts to improve the mechanical properties of degradable polymers have involved combining them with calcium phosphates such as hydroxyapatite (HA) or tricalcium phosphate (TCP) [7, 8]. In addition, the inclusion of HA in polylactide increases the bioactivity of the composite [9, 10].

The concepts of self-reinforcement and addition of calcium phosphate fillers have been combined to produce high strength, bioactive composites [11, 12]. This study investigates the initial mechanical properties and degradation characteristics of such a composite, self-reinforced polylactide containing either HA or TCP.

2. Materials

Polylactide with an L:D,L ratio of 70:30 (PLA_{70}, Boehringer Ingelheim, Germany) was used as the matrix material. It was in the form of fine white granules and had an inherent viscosity of 6.1 dl g^{-1}. Polylactide with an L:D ratio of 96:4 (PLA_{96}, Purac Biochem b.v., The Netherlands) was spun into fibers using a microextruder (Gimac, Castronno, Italy) at temperatures ranging from 190 to 265 °C, the highest temperature being at the die. The fibers were drawn by passing them through a series of rollers and furnaces at 100–125 °C, i.e. above the glass transition temperature of the fibers, to give a final draw ratio of 4.6. Two different calcium phosphates were used as the fillers, hydroxyapatite (HA, Plasma Biotal, Tideswell, UK) and tricalcium phosphate (TCP, IRC in

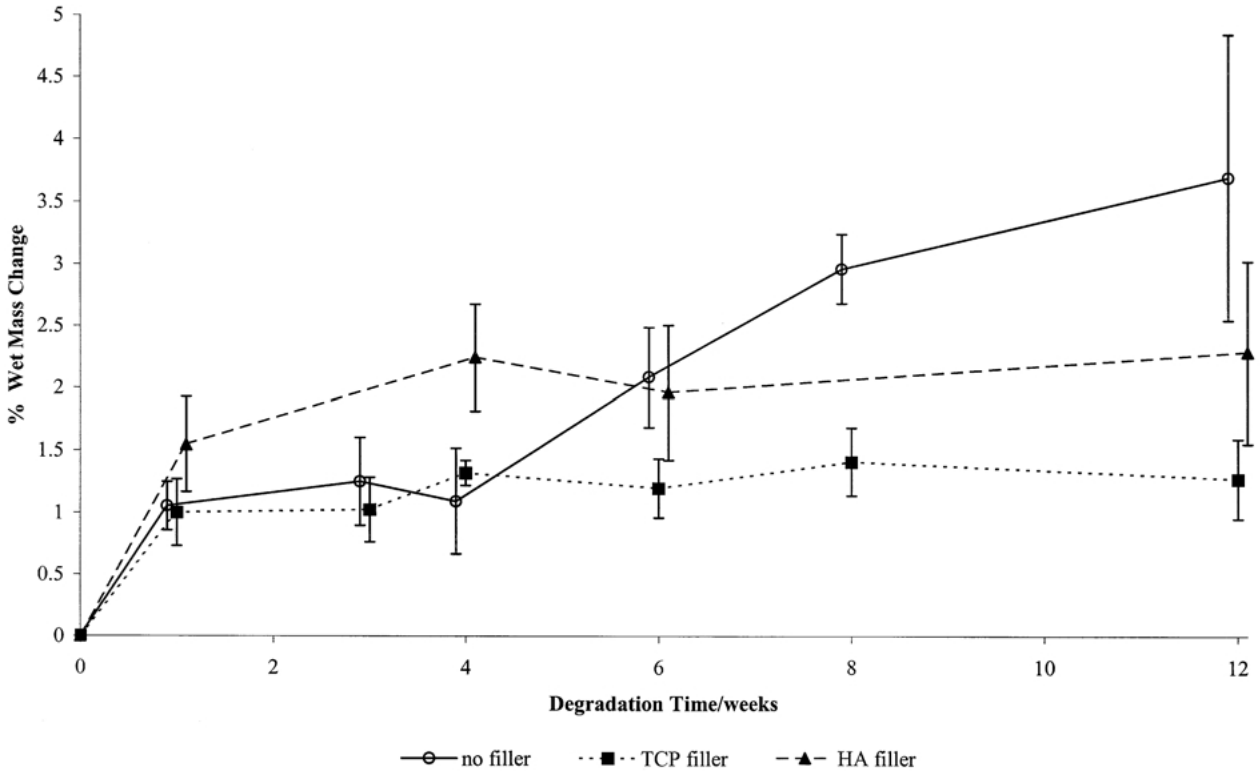

Figure 1 Percentage wet mass change versus degradation time.

Biomedical Materials, London, UK). The fillers had similar particle sizes, with $d_{0.5} = 2.99\,\mu m$ for HA and 3.44 μm for TCP. However, the specific surface areas were substantially different at 16.3 and $3.15\,m^2 g^{-1}$ respectively.

3. Methods

The composite was manufactured in a two-step process, producing a preimpregnated sheet (prepreg), followed by compression molding. PLA_{70} was dissolved in acetone ($40\,g\,l^{-1}$) and either no filler or 70 wt % HA or TCP were added, stirring to give a homogeneous mix. A prepregger (Research Tool Corporation, Michigan, USA) was used to pull bundles of PLA_{96} fiber through the matrix solution before winding onto a rotating drum. The resulting prepreg was dried in a vacuum oven at room temperature, to ensure complete evaporation of the acetone, and stored over silica.

Nine layers of prepreg (lay up 0°/0°/0°/90°/0°/90°/0°/0°/0°) were compression molded into plates at 150 °C using a hydraulic press (Palamine, Haverhill, UK). A pressure of 8 MPa was applied while the mold was heated and cooled, while 20 MPa was applied for 1 min once a temperature of 150 °C had been reached. Plates were 1–2 mm thick and were cut into samples $100 \times 10\,mm^2$. All samples were sterilized by gamma irradiation prior to testing.

Four point bend testing was carried out using an Instron 4644 test machine (Instron, High Wycombe, UK) at a strain rate of $5\,mm\,min^{-1}$ and a 2 : 1 support : loading span ratio. Five samples for each variable (no filler, HA filler and TCP filler) were tested until a cross-head displacement of 15 mm was reached. Only a few samples fractured, but all yielded allowing a flexural modulus and yield strength to be calculated. Analysis of variance was carried out to assess the statistical significance of the results.

Samples were degraded for up to 12 weeks in simulated body fluid (SBF K9) [13] with the five repeat specimens degraded together in 150 ml SBF at 37 °C. Prior to degradation, the mass of all samples was recorded. SBF was changed every three weeks. At 1, 3, 4, 6, 8 and 12 weeks samples were removed, surface dried and reweighed. The difference in the wet mass and the initial mass was recorded as a measure of water uptake by the samples. Samples were then dried in a vacuum oven at room temperature until their weight remained stable. This drying allowed the mass loss of the sample to be recorded. Finally, samples underwent four point bend testing as described above.

4. Results

Fig. 1 shows the percentage increase in wet mass of the samples after immersion in SBF for up to 12 weeks, giving an indication of the water uptake. Error bars represent one standard deviation. Until four weeks the samples containing HA absorb more water than those containing TCP or no filler, but after six weeks of degradation, the plain samples absorb the most water. Fig. 2 shows the percentage decrease in sample mass after drying, representing the mass of sample that has been lost by degradation following immersion in SBF. After an initial mass decrease, the mass of the composite samples remains constant up to eight weeks. After eight weeks, the dry mass of the plain samples decreases

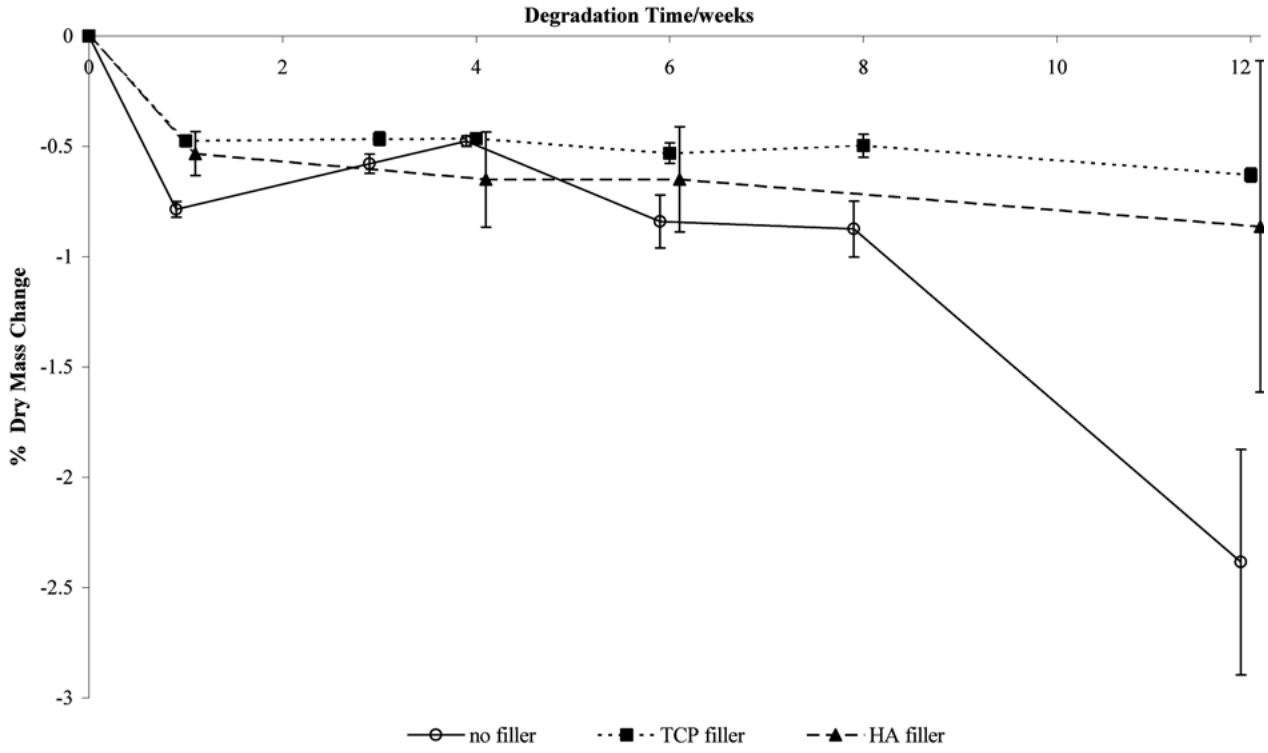

Figure 2 Percentage dry mass change versus degradation time.

sharply and the mass of the samples containing TCP decreases to a lesser extent.

Figs 3 and 4 show how the flexural modulus and yield stress change over the 12-week period. Again, error bars represent one standard deviation. Initially, the modulus of the unfilled material is significantly lower ($p < 0.01$) than the two filled materials, a trend that is apparent for the whole degradation time. By the sixth week, the moduli of the filled materials increase significantly ($p < 0.05$) by 15–20%. Thereafter, the moduli for each material remain constant until the twelfth week of degradation, when the flexural modulus of the samples containing no filler has significantly decreased ($p < 0.01$). No such decrease is seen in the samples containing HA or TCP filler. The initial flexural yield strength of the unfilled samples is significantly lower ($p < 0.01$) than the filled samples. The two filled materials show a constant flexural yield stress over the 12 weeks while the yield stress of the unfilled material drops at week 12 ($p < 0.001$).

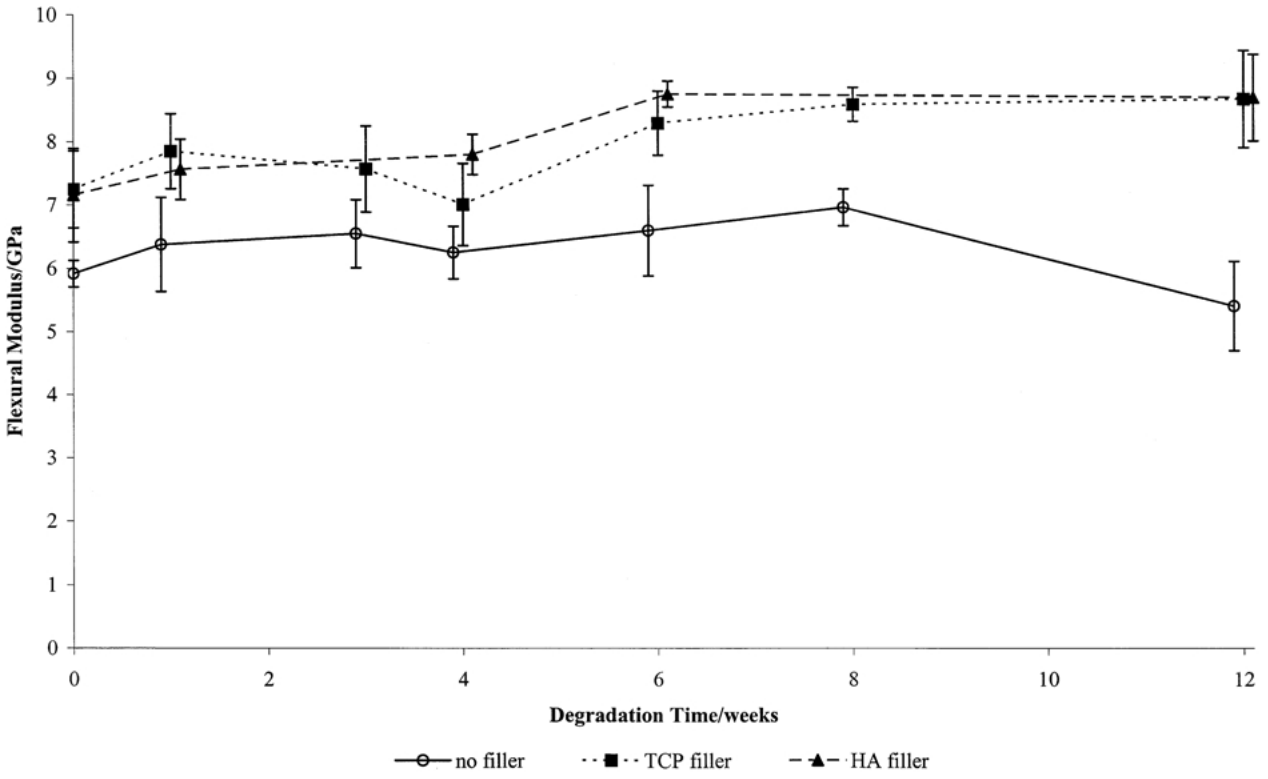

Figure 3 Flexural modulus versus degradation time.

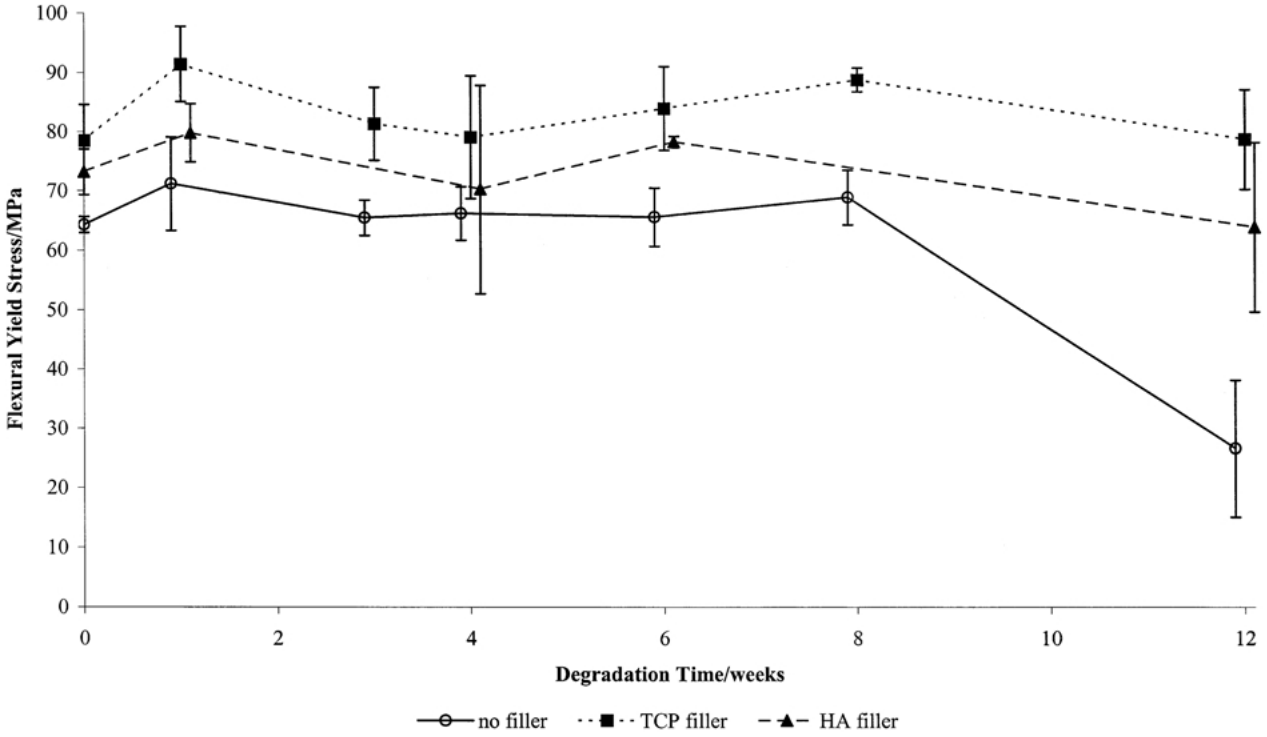

Figure 4 Flexural yield stress versus degradation time.

5. Discussion

The results of this 12-week degradation study indicate that the degradation rate of self-reinforced polylactide is decreased by the addition of a calcium phosphate filler. This behavior is contrary to initial expectations since it was thought that fluid would be absorbed into the composite via the particle/matrix interface, accelerating hydrolysis. This theory is partially supported by the data in Fig. 1 where the samples containing HA were found to absorb the most water up to four weeks. The HA had five times the specific surface area of the TCP so there were more pathways for water to be drawn into the composite. Throughout the 12 weeks, the amount of water taken up by the samples containing HA was greater than for those containing TCP.

However, during the first half of the degradation period, the amount of water taken up by the composite was not related to the mass loss (Fig. 2). Until week 6, all the samples showed a minimal decrease in mass, a commonly reported phenomenon [14, 15] that is attributed to a delay in the leaching out of low molecular weight fragments, which are the products of hydrolysis. By week 12, a decrease was seen in the dry mass of the unfilled samples resulting from an increase in water uptake. As more of the polymer was hydrolyzed, the ability of oligomers to leach out of the composite increased. More water was then able to enter the composite, resulting in an increased hydrolysis rate. The samples containing HA filler showed a smaller increase in mass loss by week 12, although this was greater than the mass loss shown by the samples containing TCP. This difference is likely to be due to the differences in surface area of the two ceramics rather than differences in their degradation rates (it has been shown that TCP degrades 3–12 times faster than HA [16]). If the degradation rate of the ceramic were a dominant factor then it would be expected that the TCP-containing samples would show a greater loss of mass than the HA-containing samples. This study is to be continued until 24 weeks of degradation, by which time such effects may be seen.

Fig. 3 illustrates that adding filler particles to a polymer increases its modulus, as is expected. This increase gave a flexural modulus for the composite similar to that of cortical bone, suggesting that the composite will be mechanically suitable for use in bone fracture repair. Similarly, the flexural yield stresses (Fig. 4) were higher for the filled than the unfilled samples and were within the range of values found for cortical bone, an observation that agrees with other work [11]. An initial increase in modulus and yield stress after immersion in SBF can be attributed to the leaching of any remaining monomer or low molecular weight fragments which act as plasticizers. By week 12, a significant decrease in flexural modulus and yield stress was seen for the unfilled samples. These decreases corresponded to the increased mass loss and water uptake and gives further evidence that degradation was faster in the unfilled material. An uncomplicated fracture takes around 12 weeks to heal and the results of the four point bend tests show that HA or TCP filled self-reinforced polylactide remains strong and stiff enough to support the bone during this healing period.

6. Conclusions

- Adding HA or TCP particles to the material increased the flexural modulus and yield stress to values within the range of those reported for

cortical bone. In addition, the flexural modulus and yield stress were maintained over a 12 week *in vitro* period when filler particles were added to the composite.

- Adding calcium phosphate filler particles to the composite system had no effect on the degradation of the material, as measured by water uptake and mass loss, in SBF for up to 6 weeks. However, by 12 weeks, the samples containing no fillers absorbed more water and showed greater mass loss than those containing HA or TCP fillers.
- The samples containing no filler showed a significant decrease in flexural modulus and yield strength at week 12.

Acknowledgments

The IRC in Biomedical Materials is grateful for core funding and for a studentship (N.C.B.) from EPSRC (UK). The authors are grateful for the assistance of Ms A. Sjölund in making the PLA_{96} fibers, Mr C. Langdown in manufacturing the prepreg and Mr S. Ke in providing and characterizing the TCP.

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Received 14 May
and accepted 21 May 2001