

Mechanical Properties of a Degradable Phosphate Glass Fibre Reinforced Polymer Composite for Internal Fracture Fixation

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Abstract

This paper reports on the mechanical properties and pH upon degradation of phosphate glass fibre reinforced methacrylate-modified oligolactide. Phosphate glass fibres of the composition 51.04 P₂O₅ - 21.42 CaO - 25.51 Na₂O - 2.03 SiO₂ (mol %) were produced by a crucible spinning technique. Fibres were embedded into a matrix of a degradable organic polymer network based on methacrylate-modified oligolactide; samples with and without addition of CaCO₃ for pH control were produced. pH during degradation in physiological NaCl solution could be increased to up to 6.5 by addition of 20 wt% calcium carbonate to the fibre composites. pH in Tris buffer solution was about 7.11. Mechanical properties of dry specimens were investigated during 3-point bending tests and gave elastic moduli in the range of cortical bone (15 to 20 GPa). However, addition of calcium carbonate decreased tensile strength of the fibre composites and resulted in brittle fracture behaviour, while CaCO₃-free composites showed a fibrous fracture mode. Control of pH and degradation is a requirement for obtaining a fracture fixation device with degradation properties matching *in vivo* requirements. Results show that addition of CaCO₃ is suitable for controlling the pH during degradation of metaphosphate glass polymer composites.

Keywords

phosphate glass fibres; fibre composite; degradation; mechanical properties

1. Introduction

Degradable polymers, such as polyesters, are currently used as sutures or degradable fracture fixation materials such as screws. Their main advantages over metallic implants are avoidance of a second operation to remove the fixation device and avoidance of stress-shielding by a gradual load transfer from the degrading polymer to the regenerating bone. However, their lower stiffness (poly(lactic acid) (PLA) screws: around 3 GPa [1]) in comparison to bone (17-26 GPa [2]) may allow too much bone motion for satisfactory healing and reinforcement therefore is essential. Reinforcement by glass fibres is of interest as the fibres maintain stability and mechanical properties during later states of polymer degradation, and anisotropic materials, such as fibre-composites, offer superior strength and stiffness in comparison to isotropic materials.

The reinforcing phase may also act as to control the degradation of the polyester. Hydrolysis starts with the intrusion of water into the polymer bulk and is catalysed by acidic media. If hydrolysis is slow compared to diffusion, the complete cross section of a polymer matrix is degraded, and as the degradation products of polyesters lower the pH of the surroundings, they cause auto-catalysis in thick sections that leads to rapid deterioration of the polymer matrix and its mechanical properties [3-5]. Incorporating inorganic fillers which neutralise the pH is one way of controlling this degradation process [6].

We previously produced a phosphate glass fibre reinforced methacrylate-modified oligolactide using fibres made out of phosphate invert glasses [7]. The structure of phosphate invert glasses consists of small phosphate units (*e.g.* pyrophosphate) [8], which results in an increased crystallization tendency of the melt and makes drawing of glass fibres challenging. Metaphosphate glasses, on the other hand, consist of long phosphate chains [9], which facilitates drawing of glass fibres and results in anisotropy of the fibres [10]. However, as metaphosphate glasses give an acidic pH in aqueous solution [11], a neutralising filler needs to be added in order to control polymer degradation.

In this work, glass fibres of phosphate glasses in the system P_2O_5 -CaO- Na_2O - SiO_2 were produced by a crucible spinning technique. Fibres were embedded into a matrix of a degradable organic polymer network based on methacrylate-modified oligolactide [12,13]; calcium carbonate was added in order to control the pH. Mechanical properties of the composites and pH in physiological NaCl solution were investigated.

2 Experimental Procedure

2.1 Preparation of fibres

A glass with a composition of 51.04 P_2O_5 - 21.42 CaO - 25.51 Na_2O - 2.03 SiO_2 (mol %) was melted in a silica crucible at 1100 °C for 1 h. The melt was cast onto a copper block and quenched by pressing another copper block onto it.

The fibres were drawn using a drawing rig described previously [14]: a platinum crucible (80 mm length and 24 mm inner diameter) with a nozzle (down pipe) at the bottom was located inside a resistance heated furnace; the nozzle had a length of 20 mm and an inner diameter of 1 mm. A thermocouple was placed inside the crucible while another was located at the nozzle. 45 g of glass were placed in the crucible and heated up to a temperature of 1020 °C. The melt was kept for 30 min at this temperature, and then it started to drop through the nozzle. The drop was taken and drawn manually to a fibre and put on the drum which was located below in line with the crucible. The drum was set into rotation using a variable rotation speed in the range from 200 to 1400 min^{-1} , which is equivalent to drawing speeds ranging from 1.43 to 10.01 $m s^{-1}$. The fibre diameter was measured during the drawing procedure using a laser-beam fibre diameter measuring device (ODAC, Zumbach Ltd) with an accuracy of $\pm 1 \mu m$. The results of these online

measurements were in agreement with microscopic determinations of the fibre diameter. The as drawn fibres were stored in a desiccator.

2.2 Preparation of composites

A dianhydro-D-glucitol bis[di(lactoyl)methacrylate] macromer was used as polymer network forming component. Macromer synthesis was performed in a two-step process as described earlier [15,16]. For the fabrication of fibre reinforced composites, the fibres were cut in fibre bundles about 30 cm in length, bunched and soaked in macromer/HEMA/dibenzoyl peroxide mixture before polymerization, and placed in a custom made mould which was thinly coated with glycerol. This mould consisted of five glass plates of 30 x 5 cm² located between two glass plates of 50 x 30 cm². The size of the samples was 2.5 mm x 2.0 mm x 50 cm. Macromer-soaked fibres were cured inside the mould for 1 h at 100°C. After curing, the fibre composites were cut into pieces of about 20 cm length and the surface was smoothed by grinding.

2.3 Characterisation of composites

2 g of sample (glass fibres, fibre composites without calcium carbonate and composites with 20 wt% CaCO₃) were placed in 200 mL of physiological sodium chloride solution (0.9 wt% NaCl) and kept at 37°C. The pH of this solution was measured every 24 h for ten days; the solution was exchanged daily. Experiments were performed in triplicates.

Tris buffer solution was prepared by dissolving 15.090 g tris(hydroxymethyl)aminomethane (Sigma-Aldrich) in ca. 800 mL deionised water, adding 44.2 mL 1 M hydrochloric acid (Sigma-Aldrich), heating to 37°C over night, adjusting the pH to 7.26 using 1 M hydrochloric acid using a pH meter (Oakton Instruments, NL) and filling to a total volume of 2000 mL using deionised water. Tris buffer solution was kept at 37°C. 50 mL solution were used per 75 mg sample. Samples were placed in an orbital shaker at 37°C at an agitation rate of 60 Hz for 10 days. The pH of this solution was measured every 24 h for ten days, solution was not exchanged during the time of the experiment. After 10 days, samples were dried at 37°C and the weight loss was determined. Experiments were performed in quadruplicates.

For mechanical testing, diameters of the fibres in the composites were varied. Elastic modulus and tensile strength of dry fibre reinforced composite with and without 20 wt% CaCO₃ were determined during 3-point bending tests using a hydraulic testing machine (UPM 1445, Zwick GmbH, Germany). For elastic modulus samples about 200 mm in length were studied; test speed was 10 mm/min and span length 100 mm. For each material at least three specimens were tested. Afterwards the samples were cut into shorter pieces (about 45 mm in length) and tensile strength was determined: test speed was 1 mm/min and span length 40 mm. For each material at least 11 specimens were tested.

For scanning electron microscopy (SEM), fibre composites were clamped into a small 3-point bending device. The fibre composite was bent, carbon sputter-coated and lower secondary electron images of the fracture were obtained using a Jeol 7001F with Schottky emitter.

2.4 Statistical data analysis

Normal distribution [17] of tensile strength measurements was tested using Shapiro-Wilk test (OriginPro7.5, OriginLab Corporation, Northampton, MA, USA). Influence of CaCO₃ addition on elastic modulus and tensile strength was investigated using two-sample *t*-test (OriginPro7.5, OriginLab Corporation, Northampton, MA, USA). $p < 0.05$ was considered significant. Results are presented as mean \pm standard deviation (SD).

3 Results

3.1 Fibre diameter

In Table 1 initial fibre diameters are shown as a function of drawing speed; fibre diameters decreased with increasing drawing speed. As reported previously, the mass flow through the nozzle does not depend on the drawing speed [14] but is a function of the hydrostatic pressure, and due to the experimental set-up the mass flow is a function of time. Therefore the fibre diameter decreased during the course of the fibre drawing experiment, and the experiment was stopped after 4 min. At that point the decrease in diameter was less than 10% compared to the initial diameter.

Table 1: Fibre diameters as a function of the drawing speed.

Sample	Drawing speed min^{-1}	Drawing speed $\text{m}\cdot\text{s}^{-1}$	Fibre diameter μm
A	200	1.43	60
B	400	2.15	44
C	600	4.29	32
D	800	5.72	33
E	1000	7.15	30
F	1200	8.58	27
G	1400	10.01	26

3.2 pH in physiological solutions

In Fig. 1a, the pH-values of the glass fibres, the glass fibre reinforced composite, and the glass fibre reinforced composite containing CaCO_3 in 0.9 wt% NaCl solution are shown as a function of time. The glass fibres gave an initial pH of about 2, which increased to 2.5 at day 5 and remained constant over the following 5 days. The glass fibre reinforced composite gave an initial pH of 2.5, which increased to around 5 after 4 days and remained constant until the end of the experiment. The fibre reinforced polymer matrix composite with 20 wt% CaCO_3 gave an initial pH of 4.6 which increased to pH 6 at 3 days and pH 6.5 at 10 days.

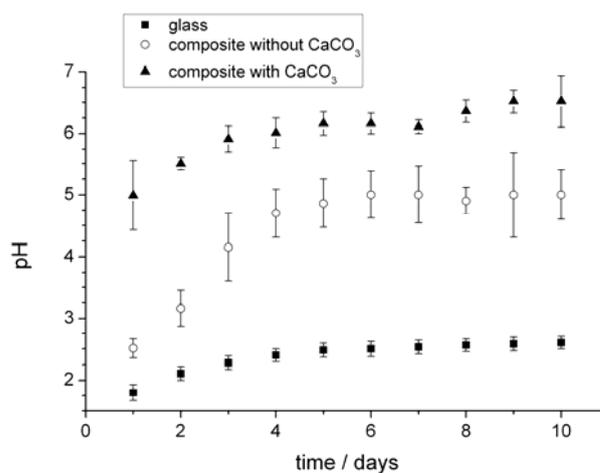


Figure 1: Changes in pH (\pm SD) of the dissolution medium as a function of degradation time and sample composition: (a) glass fibres, fibre composites with and without addition of calcium carbonate in 0.9 wt% NaCl solution and fibre composites with addition of calcium carbonate in Tris buffer solution, (b) fibre composites with addition of calcium carbonate in Tris buffer solution.

pH of Tris buffer solution was 7.26. After adding CaCO_3 -containing fibre composites, pH decreased and from day 5 stayed constant at a pH of about 7.11. Weight loss of the samples over 10 days was (48 ± 1) wt%.

3.3 Mechanical properties of the composites

Fibre composites with and without calcium carbonate show mean elastic moduli between 15 and 20 GPa (Fig. 2). There is no significant influence of fibre drawing speed (*i.e.* fibre diameter) on elastic modulus. For fibre composites with fibres drawn at 800 min⁻¹ there was a significant difference between composites with and without CaCO₃ (two-sample *t*-test, $p < 0.05$); for all other fibre diameters addition of CaCO₃ had no significant influence on the elastic modulus of the composites.

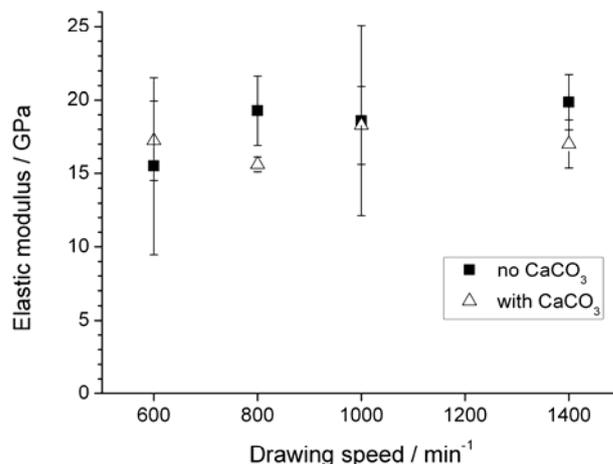


Figure 2: Elastic modulus (\pm SD) of fibre composites with and without addition of calcium carbonate vs. fibre drawing speed.

Results of tensile strength measurements were normally distributed at the 0.05 level. Fig. 3 shows tensile strengths of fibre composites with and without CaCO₃. Addition of CaCO₃ decreased the tensile strength of the composites; apart from composites with fibres drawn at a speed of 400 min⁻¹ the difference was statistically significant (two-sample *t*-test, $p < 0.05$).

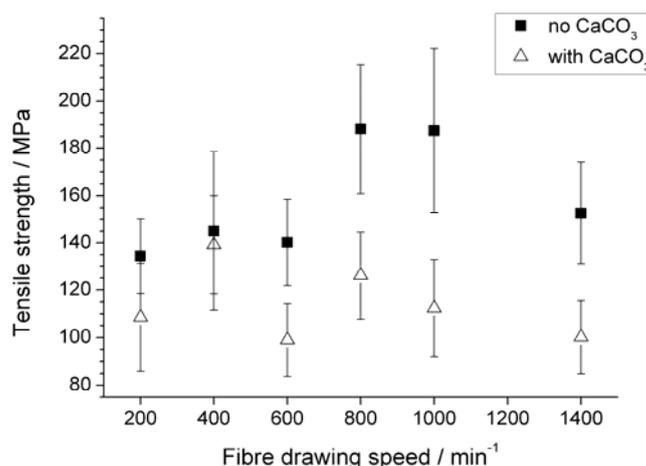


Figure 3: Tensile strength (\pm SD) of fibre composites with and without addition of calcium carbonate vs. fibre drawing speed.

Fracture curves of composites without CaCO₃ show a gradual decrease in stress after fracturing, corresponding to a fibrous fracture mode (Fig. 4), while addition of CaCO₃ resulted in brittle fracturing of the composites (Fig. 5) with the stress curves dropping sharply after fracture.

Fig. 6 shows SEM micrographs of fibre composites without CaCO_3 during 3-point bending: the images show a fibre composite with a crack; within that crack both fractured and intact fibres are visible which bridge the crack. By contrast, fibre composites containing 20 wt% CaCO_3 fractured completely when clamped for SEM imaging; Fig. 7 shows a fracture surface: glass fibres are still present but have broken close to the fracture surface.

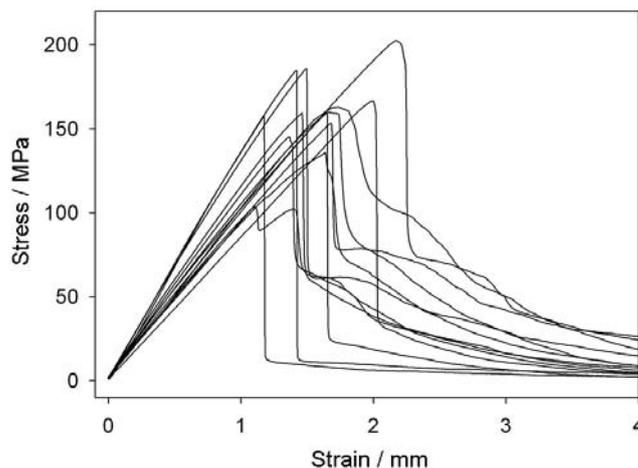


Figure 4: 3-point bending strength of fibre composites without addition of calcium carbonate (fibres drawn at 1400 min^{-1}). Curves show fibrous fracture mode.

4 Discussion

Phosphate glasses are water soluble, and their degradation rate can be adjusted by altering their composition. Pyrophosphate glasses, which consist mainly of small phosphate groups (phosphate dimers and orthophosphate), have been shown to give a neutral to slightly basic pH in aqueous solutions. By contrast, poly- and metaphosphate glasses have a phosphate chain structure and may therefore be of special interest for fibre production. A disadvantage of using metaphosphate glasses is, however, that they tend to give an acidic pH in aqueous solutions and degrade much faster than pyrophosphate glasses [11]. In degradable polymer composites controlling the pH therefore is important, as an acidic pH can result in rapid deterioration of the polymer [3-5] and can also cause inflammation *in vivo*.

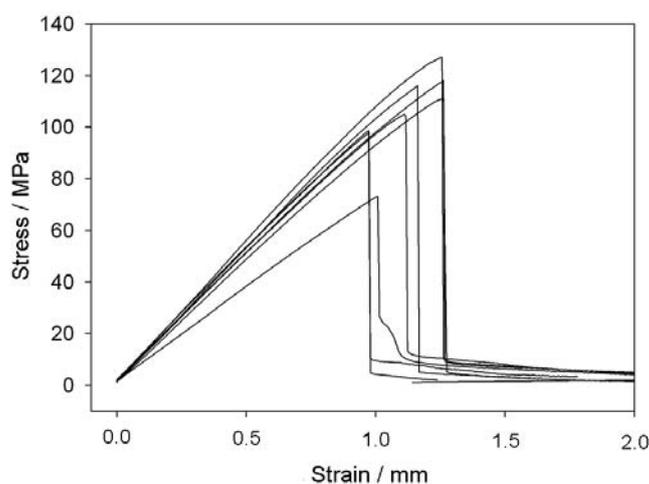


Figure 5: 3-point bending strength of fibre composites with addition of calcium carbonate (fibres drawn at 1400 min^{-1}). Curves show brittle fracturing.

We prepared composites by incorporating continuous metaphosphate glass fibres into a degradable polymer matrix of a methacrylate-modified oligolactide. In order to control the pH, we incorporated calcium carbonate into some of the

composites. While the glass fibres gave a pH between 2 and 2.5 in NaCl solution and CaCO₃-free composites gave a pH rising from 2.5 to 5 over ten days, incorporation of calcium carbonate resulted in a pH close to neutral (pH = 6.5 at day 10). This shows that incorporation of calcium carbonate into the composite buffered the pH of the dissolution medium. When testing the pH in Tris buffer solution, the pH dropped from 7.26 to 7.11 over five days and then stayed constant at that pH for the remaining time of the experiment.

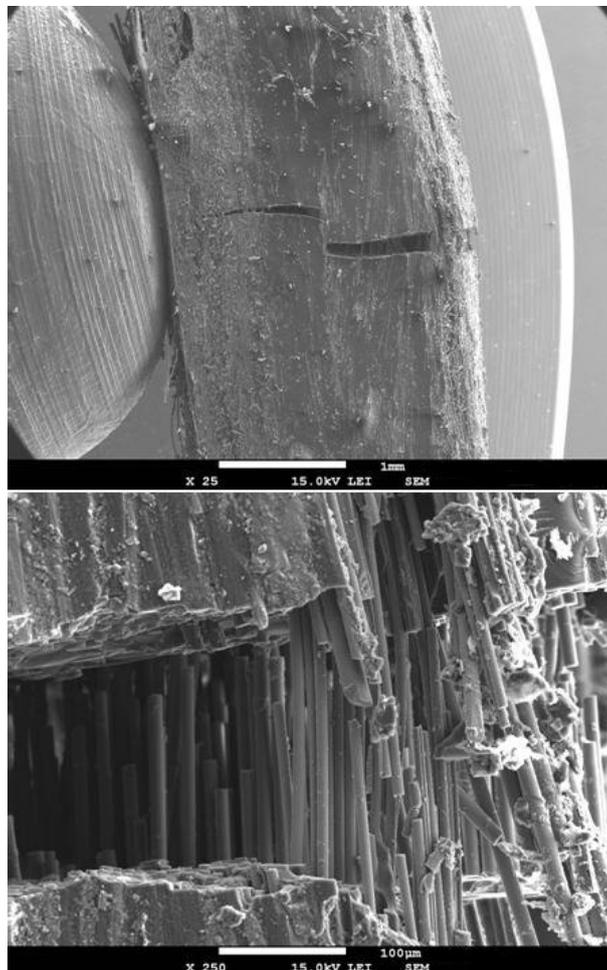


Figure 6: SEM micrograph of fibre composite without CaCO₃: fracture during 3-point bending.

Metaphosphate glass fibre polymer composites were shown to give an acidic pH [18,19] upon degradation: Ahmed *et al.* used glasses in the metaphosphate composition range for fabrication of degradable glass fibre-reinforced composites using poly(lactic acid) [19] and poly- ϵ -caprolactone [18]. Their results showed very fast degradation of the fibres, resulting in pH 4. pH only increased to neutral after the fibres had completely degraded and only the polymer matrix contributed to the pH (at 350 h, *i.e.* 15 days). Our results show that neutralising inorganic fillers, such as calcium carbonate are therefore of interest for use in metaphosphate glass fibre polymer composites, as they can successfully increase the pH during degradation compared to the materials without neutralising filler. However, degradation times are still short with the samples showing a weight loss of 48% after 10 days. Although times for bone healing (and subsequently requirements for degradation of the implant) depend on the defect, bone formation and full replacement of the degradable implant *in vivo* can take from 9 months and up to 3 years [20], and during this time the implant needs to provide at least partial mechanical support.

While addition of calcium carbonate had a beneficial effect on the pH during degradation of the composites, it affected mechanical properties of the composites: composites both with and without addition of CaCO₃ showed elastic moduli in

the range of cortical bone (15 to 20 GPa); fibre diameter or addition of calcium carbonate had no significant effect on elastic moduli of the composites. However, addition of calcium carbonate significantly affected the tensile strength and the fracture behaviour of the composites: it reduced the tensile strength of the composites and also resulted in brittle fracture of the composites, while CaCO_3 -free composites showed fibrous fracturing. During fracture of CaCO_3 -free fibre composites, glass fibres bridged the crack and thereby still provided some stability during fracturing, which explains the fibrous fracture mode. Fibre composites containing CaCO_3 , on the other hand, broke completely when clamped for SEM imaging. At the fracture site glass fibres are still visible but broke near the fracture surface and apparently did not delay fracture of the composite. This can be explained by the fact that incorporation of CaCO_3 induced defects into the structure of the composites, resulting in a decrease in strength. While in the literature incorporation of inorganic fillers was shown to increase the compressive strength of degradable polymers such as poly(lactic acid) [6] and did not affect elastic moduli of the composites in our study, it seems to have a negative effect on tensile strength and fracture mode.

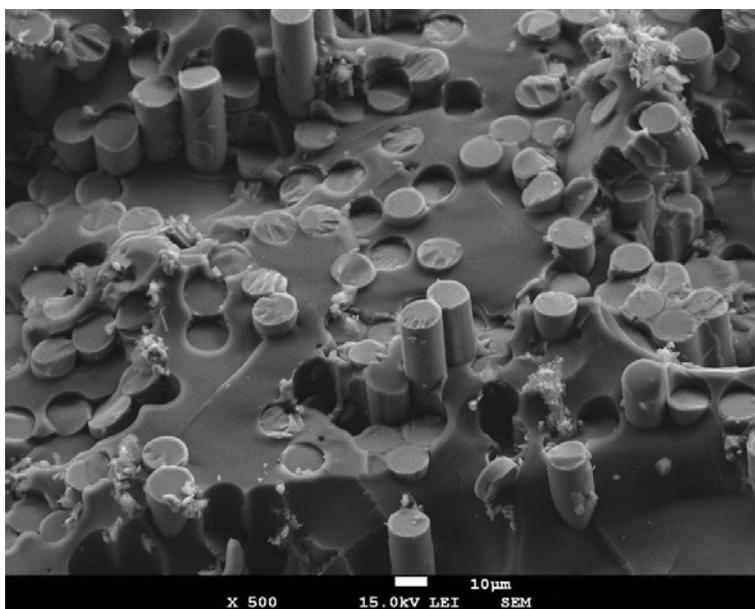


Figure 7: SEM micrograph of fibre composite with CaCO_3 : fracture surface after 3-point bending.

In summary, while addition of calcium carbonate successfully increased the pH during degradation towards a more neutral pH and composites gave elastic moduli similar to cortical bone, degradation times of the composites were still short, and addition of calcium carbonate negatively affected the fracture behaviour, causing brittle fracturing and reducing the tensile strength. While neutralising fillers were shown beneficial in composites, their use in fibre composites might therefore be limited. Future research will therefore focus on fibre composites using phosphate invert glasses which were shown to give a neutral pH upon degradation and longer degradation times.

Conclusion

Metaphosphate glass fibre polymer composites for use as internal fracture fixation devices were produced, and composites with addition of calcium carbonate as a neutralising inorganic filler show an improved pH during degradation (pH increased towards neutral) compared to composites without calcium carbonate. Controlling the pH is important as polymer degradation is acid catalysed and a drop in pH can result in fast degradation of the polymer matrix and mechanical properties. As low pH values can also trigger inflammation *in vivo*, buffering the pH of degradable

implant materials can therefore also decrease the risk of inflammation. Tensile strength of the composites was decreased by incorporation of calcium carbonate, but elastic moduli were not affected and were in the range of cortical bone.

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