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Effect of Si and Fe doping on calcium phosphate glass fibre reinforced polycaprolactone bone analogous composites

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ABSTRACT

Reinforcing biodegradable polymers with phosphate-based glass fibres (PGF) is of interest for bone repair and regeneration. In addition to increasing the mechanical properties, PGF can also release bioinorganics, as they are water soluble, a property that may be controllably translated into a fully degradable composite. Herein, the effect of Si and Fe on the solubility of calcium-containing phosphate-based glasses (PG) in the system ($50P_2O_5$–40CaO–$(10-x)SiO_2$–xFe_2O_3, where x = 0, 5 and 10 mol.%) were investigated. On replacing SiO_2 with Fe_2O_3, there was an increase in the glass transition temperature and density of the PG, suggesting greater crosslinking of the phosphate chains. This significantly reduced the dissolution rates of degradation and ion release. Two PG formulations, $50P_2O_5$–40CaO–$10Fe_2O_3$ (Fe10) and $50P_2O_5$–40CaO–$5Fe_2O_3$–$5SiO_2$ (Fe5Si5), were melt drawn into fibres and randomly incorporated into polycaprolactone (PCL). Initially, the flexural strength and modulus significantly increased with PGF incorporation. In deionized water, PCL–Fe_5Si_5 displayed a significantly greater weight loss and ion release compared with PCL–Fe10. In simulated body fluid, brushite was formed only on the surface of PCL–Fe_5Si_5. Dynamic mechanical analysis in phosphate buffered saline (PBS) at 37 °C revealed that the PCL–Fe10 storage modulus (E') was unchanged up to day 7, whereas the onset of PCL–Fe_5Si_5 E' decrease occurred at day 4. At longer-term ageing in PBS, PCL–Fe_5Si_5 flexural strength and modulus decreased significantly. MC3T3-E1 preosteoblasts seeded onto PCL–PGF grew up to day 7 in culture. PGF can be used to control the properties of biodegradable composites for potential application as bone fracture fixation devices.

1. Introduction

Composites based on biodegradable polymers and bioactive ceramics have been extensively considered as bone analogous materials [1]. As alternatives to metals, they present the potential for reduced stress shielding, and would obviate additional surgical intervention [2]. Degradable synthetic polymers such as poly(α-hydroxy-acid esters), e.g. polylactic acid (PLA), polyglycolic acid (PGA) and their copolymers (PLGA) [3], as well as polycaprolactone (PCL) [4], have been considered as matrices. Apart from their lack of bioactivity, these polymers do not have the capacity to withstand certain load-bearing conditions. In order to overcome these limitations, bioactive calcium phosphate particulates have been incorporated into these polymeric matrices [5,6].

It is well recognised that the addition of bioactive glasses and ceramics into a polymeric matrix should improve the properties of the composites. However, while particulate composites are easily manufactured, fibre-reinforced composites have been shown to result in a greater increase in their mechanical properties. For example, Jiang et al. [7] investigated bioactive glass fibre incorporated PCL and showed an improvement in the flexural strength and modulus of the composites. Foams of hydroxyapatite (HA) short fibre reinforced PLGA have also shown enhanced compressive yield strength [8]. Furthermore, since the composition, content and solubility of the filler component are parameters that can influence composite properties, their tailoring is essential for bone repair and regeneration. However, not all calcium phosphate materials (e.g. silicate-based glasses or HA) provide controlled solubility properties with either the bone regeneration rate or degradation of the matrix.

Phosphate-based glasses (PG) may be a potential alternative inorganic phase for the purpose of producing composites of controllable degradation [9,10]. The solubility of PG can be predicted and controlled through their chemistry [11–13]. In addition, their structural polymeric nature allows them to be easily drawn into fibres [14], which could result in a mechanical reinforcing effect when incorporated into a polymer matrix. It has been shown that PCL–PGF ($50P_2O_5$–50CaO) composites yielded flexural strength and modulus values approaching 30 MPa and 2.5 GPa, respectively,

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